

Vaughn Hagerty
Public Information Officer
235 Government Center Drive
Wilmington, NC 28403
910-332-6704
vaughn.hagerty@cfpua.org

Enclosed find records responsive to your records request referenced in the attached inquiry.

Note that I am unable to determine where or how your original request was submitted. In addition, this request was forwarded by our Customer Service Department. Each of these contributed to the delay in fulfilling your request.

In the future, please submit requests for records to Cape Fear Public Utility Authority to:
Communications@cfpua.org.

Regards,

A handwritten signature in black ink, appearing to be "V. Hagerty", written over a faint, circular, dotted watermark or background.

Vaughn Hagerty

Cape Fear Public Utility Authority
North Carolina Public Records Law Office
235 Government Center Drive
Wilmington, NC 28403

As of 7/9

July 9, 2019

This is a follow up to a previous request:

To Whom It May Concern:

I wanted to follow up on the following North Carolina Public Records Law request, copied below, and originally submitted on Sept. 19, 2018. Please let me know when I can expect to receive a response.

Thanks for your help, and let me know if further clarification is needed.

Filed via MuckRock.com
E-mail (Preferred): 61294-24130404@requests.muckrock.com

For mailed responses, please address (see note):
MuckRock News
DEPT MR 61294
411A Highland Ave
Somerville, MA 02144-2516

PLEASE NOTE: This request is not filed by a MuckRock staff member, but is being sent through MuckRock by the above in order to better track, share, and manage public records requests. Also note that improperly addressed (i.e., with the requester's name rather than "MuckRock News" and the department number) requests might be returned as undeliverable.

On Sept. 19, 2018:
Subject: North Carolina Public Records Law Request: GenX Report Documents
To Whom It May Concern:

Pursuant to the North Carolina Public Records Law, I hereby request the following records:

All agency records (including, but not limited to letters, correspondence, tape recordings, notes, data, memoranda, reports, email) held by Cape Fear Public Utility Authority related to CFPUA Vice Chair Jennifer Adams' report "Review of GenX Response," which reviewed the "GenX issue" and the appropriateness of CFPUA's response and was issued in June 2017.

This requests includes but is not limited to all documents utilized in Ms. Adams' report including:

Documents voluntarily provided by CFPUA employees and other government employees, documents provided by the private companies involved in these events, and public documents available on the internet and elsewhere. We also requests records related to interviews with CFPUA officials and employees, Chemours officials and other

persons involved in these events.

If you determine that any portion or portions of this request cannot be fulfilled as promptly as any other portion of this request, we ask that you first fulfill whatever portion of this request you can fulfill within 10 business days and then fulfill the remainder of the request as promptly as possible.

We are happy to work with your office to make this request as simple as possible and eliminate unnecessary work. Please contact us before you incur labor costs or the use of information technology resources beyond those that your agency has already established for reproduction of the information requested. We can probably find an efficient solution that serves the public interest while minimizing your effort.

The requested documents will be made available to the general public, and this request is not being made for commercial purposes.

In the event that there are fees, we would be grateful if you would inform us of the total charges in advance of fulfilling our request. We would prefer the request filled electronically, by e-mail attachment if available or CD-ROM if not.

Thank you in advance for your anticipated cooperation in this matter.

We look forward to receiving your response to this request within 10 business days.

Sincerely,

Working Narratives

Filed via MuckRock.com

E-mail (Preferred): 61294-24130404@requests.muckrock.com

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MuckRock News

DEPT MR 61294

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EPA

IN THE UNITED STATES DISTRICT COURT
FOR THE SOUTHERN DISTRICT OF WEST VIRGINIA
CHARLESTON DIVISION

UNITED STATES OF AMERICA, and)
THE STATE OF WEST VIRGINIA,)

Plaintiffs,)

v.)

E.I. DU PONT DE NEMOURS & CO., and)
LUCITE INTERNATIONAL, INC.,)

Defendants.)

Civil Action No.

CONSENT DECREE

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Plaintiffs, United States of America, on behalf of the United States Environmental Protection Agency ("EPA"), and the State of West Virginia ("the State"), have filed a complaint in this action concurrently with this Consent Decree, alleging that Defendants, E.I. Du Pont de Nemours & Co. ("DuPont") and Lucite International, Inc. ("Lucite") (together "Defendants"), violated the Clean Air Act ("Act"), 42 U.S.C. §§ 7401-7671q, and the following provisions under the Act: the Standards of Performance for New Stationary Sources at Section 111 of the Act, 42 U.S.C. § 7411, and the New Source Performance Standards for Sulfuric Acid Plants, 40 C.F.R. Part 60, Subpart H, at §§ 60.80-60.85; the Prevention of Significant Deterioration ("PSD") of Air Quality provisions, Part C of Title I of the Act at Sections 160-169B of the Act, 42 U.S.C. §§ 7470-7492; the Title V Permit Program in Title V, Sections 502-504 of the Act, 42 U.S.C. §§ 7661a -7661c, and its implementing regulations at 40 C.F.R. Part 70; West Virginia's Title V Permit Program at W. Va. Code State R. Tit. 45 § 30; and the West Virginia State Implementation Plan provisions for PSD and minor new source review at W. Va. Code State R. Tit. 45 §§ 13 and 14.

The Complaint alleges that these violations occurred at a sulfuric acid regeneration plant ("Facility") that is owned by Lucite and operated by DuPont. The Facility is a portion of a larger plant, located at 901 West DuPont Avenue, Belle, West Virginia 25015 in Kanawha County, West Virginia.

Defendant Lucite has decided, for independent business reasons, to cease operation of the Facility as of April 1, 2010.

Neither Defendant admits any liability to the United States or the State arising out

of the transactions or occurrences alleged in the Complaint.

The Parties recognize, and the Court by entering this Consent Decree finds, that this Consent Decree has been negotiated by the Parties in good faith and will avoid litigation between the Parties and that this Consent Decree is fair, reasonable, and in the public interest.

NOW, THEREFORE, before the taking of any testimony, without the adjudication or admission of any issue of fact or law except as provided in Section I, and with the consent of the Parties, IT IS HEREBY ADJUDGED, ORDERED, AND DECREED as follows:

I. JURISDICTION AND VENUE

1. This Court has jurisdiction over the subject matter of this action, pursuant to 28 U.S.C. §§ 1331, 1345, and 1355, and Section 113(b) of the Act, 42 U.S.C. § 7413(b), and over the Parties. This Court has supplemental jurisdiction over the State law claims asserted by the State of West Virginia pursuant to 28 U.S.C. § 1367. Venue lies in this District pursuant to Section 113(b) of the Act, 42 U.S.C. § 7413(b), and 28 U.S.C. §§ 1391(b) and (c) and 1395(a), because the violations alleged in the Complaint are alleged to have occurred in, and each Defendant conducts business in, this judicial district. Solely for the purposes of this Consent Decree and the underlying Complaint, the Defendants waive all objections and defenses that they may have to the Court's jurisdiction over this action, to the Court's jurisdiction over the Defendants, and to venue in this District. The Defendants shall not challenge the terms of this Consent Decree or this Court's jurisdiction to enter and enforce this Consent Decree. For purposes of the Complaint filed by the United States and the State of West Virginia in this matter and resolved by the Consent Decree, and for purposes of entry and enforcement of this Consent

Decree, the Defendants waive any defense or objection based on standing.

2. For purposes of this Consent Decree, each Defendant agrees that the Complaint states claims upon which relief may be granted pursuant to Sections 110, 111, 113 and 502-504 of the Act, 42 U.S.C. §§ 7410, 7411, 7413 and 7661a-7661c.

II. APPLICABILITY

3. The obligations of this Consent Decree apply to and are binding upon the United States and the State, and upon each Defendant and any successors, assigns, or other entities or persons otherwise bound by law.

4. No transfer of ownership or operation of the Facility, whether in compliance with the procedures of this Paragraph or otherwise, shall relieve either Defendant of its obligation to ensure that the terms of the Decree are implemented. At least thirty (30) Days prior to such transfer, each Defendant shall provide a copy of this Consent Decree to the proposed transferee and shall simultaneously provide written notice of the prospective transfer, together with a copy of the proposed written agreement, to EPA Region III, the United States Department of Justice, and to the State of West Virginia in accordance with Section XIV of this Decree (Notices). Any attempt to transfer ownership or operation of the Facility without complying with this Paragraph constitutes a violation of this Decree.

5. Each Defendant shall provide a copy of this Consent Decree to each officer, employee, and agent whose duties might reasonably include compliance with any provision of this Decree, as well as to any contractor retained to perform work required under this Consent Decree. Each Defendant shall condition any such contract upon performance of the

work in conformity with the terms of this Consent Decree.

6. In any action to enforce this Consent Decree, neither Defendant shall raise as a defense the failure by any of its officers, directors, employees, agents, or contractors to take any actions necessary to comply with the provisions of this Consent Decree.

III. DEFINITIONS

7. Terms used in this Consent Decree that are defined in the Act or in regulations promulgated pursuant to the Act shall have the meanings assigned to them in the Act or in such regulations, unless otherwise provided in this Decree. Whenever the terms set forth below are used in this Consent Decree, the following definitions shall apply:

a. "Complaint" shall mean the complaint filed by the United States and the State in this action;

b. "Consent Decree" or "Decree" shall mean this Decree;

c. "Day" shall mean a calendar day unless expressly stated to be a business day. In computing any period of time under this Consent Decree, where the last day would fall on a Saturday, Sunday, or federal holiday, the period shall run until the close of business of the next business day;

d. "Defendants" or "each Defendant" shall mean E.I. Du Pont de Nemours & Co. and Lucite International, Inc.;

e. "EPA" shall mean the United States Environmental Protection Agency and any of its successor departments or agencies;

f. "Effective Date" shall have the definition provided in Section XIII.

g. "Facility" shall mean the sulfuric acid regeneration plant that is owned by Lucite and operated by DuPont and located at 901 West DuPont Avenue, Belle, West Virginia 25015 in Kanawha County, West Virginia.

h. "Paragraph" shall mean a portion of this Decree identified by an arabic numeral;

i. "Parties" shall mean the United States, the State, and each Defendant;

j. "Plaintiffs" shall mean the United States and the State of West Virginia;

k. "Section" shall mean a portion of this Decree identified by a roman numeral;

l. "State" shall mean the State of West Virginia;

m. "United States" shall mean the United States of America, acting on behalf of EPA.

IV. CIVIL PENALTY

8. Within thirty (30) Days after the Effective Date of this Consent Decree, Defendants shall pay the total sum of \$2,000,000.00 as a civil penalty, together with interest accruing from the date on which the Consent Decree is lodged with the Court, at the rate specified in 28 U.S.C. § 1961 as of the date of lodging. Defendants shall be jointly and severally liable for payment of the civil penalty together with interest.

9. Of the civil penalty, Defendants shall pay \$1,000,000.00 to the United

States, together with interest, by FedWire Electronic Funds Transfer ("EFT") to the U.S. Department of Justice in accordance with written instructions to be provided to Defendants, following lodging of the Consent Decree, by the Financial Litigation Unit of the U.S. Attorney's Office for the Southern District of West Virginia, 300 Virginia Street, East, Suite 4000, Charleston, WV 25301, (304) 345-2200. At the time of payment, Defendants shall send a copy of the EFT authorization form and the EFT transaction record, together with a transmittal letter, which shall state that the payment is for the civil penalty owed pursuant to the Consent Decree in United States, *et al.*, v. E.I. Du Pont Nemours & Co., *et al.* and shall reference the civil action number and DOJ case number 90-5-2-1-09251, to the United States in accordance with Section XII of this Decree (Notices); by email to acctsreceivable.CINWD@epa.gov; and by mail to:

EPA Cincinnati Finance Office
26 Martin Luther King Drive
Cincinnati, Ohio 45268

10. No later than thirty (30) Days after the Effective Date of this Consent Decree, Defendants shall also together pay a civil penalty of \$1,000,000.00 to the State in accordance with written instructions to be provided to Defendants by the State, following lodging of the Consent Decree. At the time of payment, Defendants shall send the state a copy of the EFT authorization form and the EFT transaction record, together with a transmittal letter, which shall state that the payment is for the civil penalty owed pursuant to the Consent Decree in United States, *et al.*, v. E.I. Du Pont Nemours & Co., *et al.* and shall reference the civil action number. The documents shall be sent to:

Ramona Dickson
Fiscal Office

West Virginia Department of Environmental Protection
601 57th Street SE
Charleston, WV 25304

11. Defendants shall not deduct any penalties paid under this Decree pursuant to this Section or Section VII (Stipulated Penalties) in calculating its federal, State or local income tax.

V. COMPLIANCE REQUIREMENTS

12. No later than April 1, 2010, Defendants shall cease operation of the Facility. Upon the cessation of operation of the Facility, each Defendant shall surrender all air pollution permits for the Facility to the permitting authority in the State. No later than April 10, 2010, Defendants shall submit written notification to EPA Region III and to the United States Department of Justice that they have ceased operation of the Facility and surrendered all air permits to the State. Neither Defendant shall file any application for emission reduction credits as a result of such cessation of operation. Neither Defendant shall use any emission reductions resulting from such cessation of operation in any netting calculation. Neither Defendant shall sell any emission credits obtained as a result of emission reductions resulting from such cessation of operation.

VI. REPORTING REQUIREMENTS

13. On each May 30 and November 30 following the lodging of this Consent Decree, and until termination of this Decree pursuant to Section XVI, Defendants shall submit a joint status report for the preceding 6-month period that shall describe the Defendants' actions taken and to be taken to comply with this Consent Decree. This report shall include the status

and likely target date of the cessation of operation required by the preceding Section.

14. Whenever any violation of this Consent Decree or of any applicable permits or any other event affecting either Defendant's performance under this Decree, or the performance of the Facility, may pose an immediate threat to the public health or welfare or the environment, Defendants shall notify EPA and the State orally or by electronic or facsimile transmission as soon as possible, but no later than 24 hours after either Defendant first knew or should have known of the violation or event. This notification procedure is in addition to the requirements set forth in the preceding Paragraph.

15. All reports or notices required under this Consent Decree shall be submitted to the persons designated in Section XII of this Consent Decree (Notices).

16. Each report or notice submitted by either Defendant under this Section shall be signed by an official of the submitting party and include the following certification:

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

This certification requirement does not apply to emergency or similar notifications where compliance would be impractical.

17. The reporting requirements of this Consent Decree do not relieve either

Defendant of any reporting obligations required by the Clean Air Act, the West Virginia Air Pollution Control Act or implementing regulations, or by any other federal, state, or local law, regulation, permit, or other requirement.

18. Any information provided pursuant to this Consent Decree may be used by the United States or the State in any proceeding to enforce the provisions of this Consent Decree and as otherwise permitted by law.

VII. STIPULATED PENALTIES

19. Defendants shall be jointly and severally liable for stipulated penalties to the United States and the State for violations of this Consent Decree as specified below. A violation includes failing to perform any obligation required by the terms of this Decree, according to all applicable requirements of this Decree and within the specified time schedules established by this Decree.

a. Late Payment of Civil Penalty

If Defendants fail to pay the civil penalty required to be paid under Section IV of this Decree (Civil Penalty) when due, Defendants shall pay a stipulated penalty of \$5,000 per Day for each Day that the payment is late.

b. Cessation of Operation

The following stipulated penalties shall accrue per violation per Day for each Day Defendants fail to comply with the requirements of Section V of this Consent Decree:

<u>Penalty Per Violation Per Day</u>	<u>Period of Noncompliance</u>
\$ 5,000	1st through 14th Day

\$10,000 15th through 30th Day

\$25,000 31st Day and beyond

c. Reporting Requirements. The following stipulated penalties shall accrue per violation per Day for each violation of the reporting requirements of Section VI of this Consent Decree:

<u>Penalty Per Violation Per Day</u>	<u>Period of Noncompliance</u>
\$ 250	1st through 14th Day
\$ 500	15th through 30th Day
\$1,000	31st Day and beyond

d. The following stipulated penalties shall accrue per violation per Day for either Defendant's failure to comply with any requirement, not specifically referenced in this Paragraph, of this Consent Decree, within the specified time established by or approved under this Decree:

<u>Penalty Per Violation Per Day</u>	<u>Period of Noncompliance</u>
\$250	1st through 14th day
\$500	15th through 30th day
\$1,000	31st day and beyond

20. Stipulated penalties under this Section shall begin to accrue on the Day after performance is due or on the Day a violation occurs, whichever is applicable, and shall continue to accrue until performance is satisfactorily completed or until the violation ceases. Stipulated penalties shall accrue simultaneously for separate violations of this Consent Decree.

21. Defendants shall pay stipulated penalties to the United States and the State within 30 Days of a written demand by either Plaintiff. The United States, or the State, or both, may seek stipulated penalties under this Section by sending a joint written demand to either Defendant, or by either sovereign sending a written demand to either Defendant or both Defendants, with a copy simultaneously sent to the other Plaintiff. Either the United States or the State may waive stipulated penalties or reduce the amount of stipulated penalties it seeks, in the unreviewable exercise of its discretion and in accordance with this Paragraph. Where both sovereigns seek stipulated penalties for the same violation of this Consent Decree, Defendants shall pay fifty (50) percent to the United States and fifty (50) percent to the State. Where only one sovereign demands stipulated penalties for a violation, and the other sovereign does not join in the demand within twenty (20) Days of receiving the demand, or timely joins in the demand but subsequently elects to waive or reduce stipulated penalties for that violation, Defendants shall pay the full stipulated penalties due for the violation to the sovereign making the demand less any amount paid to the other sovereign, and Defendants shall not be liable for additional stipulated penalties to the other sovereign for that violation.

22. Stipulated penalties shall continue to accrue during any Dispute Resolution, but need not be paid until the following:

a. If the dispute is resolved by agreement or by a decision of EPA or the State that is not appealed to the Court, Defendants shall pay accrued penalties determined to be owing, together with interest, to the United States and the State within thirty (30) Days of the effective date of the agreement or the receipt of EPA's or the State's decision or order.

b. If the dispute is appealed to the Court and the United States or the State prevails in whole or in part, Defendants shall pay all accrued penalties determined by the Court to be owing, together with interest, within sixty (60) Days of receiving the Court's decision or order, except as provided in subparagraph c, below.

c. If any Party appeals the District Court's decision, Defendants shall pay all accrued penalties determined to be owing to the United States and the State, together with interest, within fifteen (15) Days of receiving the final appellate court decision.

23. Defendants shall pay stipulated penalties owing to the United States in the manner set forth and with the confirmation notices required by Paragraph 9, except that the transmittal letter shall state that the payment is for stipulated penalties and shall state for which violations the penalties are being paid. Defendants shall pay stipulated penalties owing to the State in the manner set forth in Paragraph 10, except that the transmittal letter shall state that the payment is for stipulated penalties and shall state for which violations the penalties are being paid.

24. If Defendants fail to pay stipulated penalties according to the terms of this Consent Decree, they shall be liable for interest on such penalties, as provided for in 28 U.S.C. § 1961, accruing as of the date payment became due. Nothing in this Paragraph shall be construed to limit the United States or the State from seeking any remedy otherwise provided by law for Defendants' failure to pay any stipulated penalties.

25. Subject to the provisions of Section X of this Consent Decree (Effect of Settlement/Reservation of Rights), the stipulated penalties provided for in this Consent Decree

shall be in addition to any other rights, remedies, or sanctions available to the United States and the State for violation of this Consent Decree or applicable law by either Defendant or both Defendants. Where a violation of this Consent Decree is also a violation of relevant statutory or regulatory requirements, Defendants shall be allowed a credit, for any stipulated penalties paid, against any statutory penalties imposed for such violation.

VIII. DISPUTE RESOLUTION

26. Unless otherwise expressly provided for in this Consent Decree, the dispute resolution procedures of this Section shall be the exclusive mechanism to resolve disputes arising under or with respect to this Consent Decree. A Defendant's failure to seek resolution of a dispute under this Section shall preclude that Defendant from raising any such issue as a defense to an action by the United States or the State to enforce any obligation of that Defendant arising under this Decree.

27. Informal Dispute Resolution. Any dispute subject to Dispute Resolution under this Consent Decree shall first be the subject of informal negotiations. The dispute shall be considered to have arisen when either Defendant sends the United States and the State a written Notice of Dispute. Such Notice of Dispute shall state clearly the matter in dispute. The period of informal negotiations shall not exceed twenty (20) Days from the date the dispute arises, unless that period is modified by written agreement. If the Parties cannot resolve a dispute by informal negotiations, then the position advanced by the United States shall be considered binding unless, within twenty (20) Days after the conclusion of the informal negotiation period, the disputing Defendant invokes formal dispute resolution procedures as set forth below. In the event that the

United States and the State are unable to reach agreement with regard to Defendant's claim, the position of the United States shall be the Plaintiffs' final position.

28. Formal Dispute Resolution. Either Defendant may invoke formal dispute resolution procedures, within the time period provided in the preceding Paragraph, by serving on the United States and the State a written Statement of Position regarding the matter in dispute. The Statement of Position shall include, but need not be limited to, any factual data, analysis, or opinion supporting Defendant's position and any supporting documentation relied upon by Defendant.

29. The United States and/or the State shall serve its Statement of Position within forty-five (45) Days of receipt of the disputing Defendant's Statement of Position. The United States' and/or the State's Statement of Position shall include, but need not be limited to, any factual data, analysis, or opinion supporting that position and any supporting documentation relied upon by the United States. In the event that the United States and the State are unable to reach agreement among themselves with regard to the claim of the disputing Defendant, the Statement of Position served by the United States shall be the Plaintiffs' final position. If the State dissents, it may file such other pleadings expressing its position as allowed by the Court. The United States' Statement of Position shall be binding on the disputing Defendant, unless that Defendant files a motion for judicial review of the dispute in accordance with the following Paragraph.

30. A disputing Defendant may seek judicial review of the dispute by filing with the Court and serving on the United States and the State, in accordance with Section XII of

this Consent Decree (Notices), a motion requesting judicial resolution of the dispute. The motion must be filed within ten (10) Days of receipt of the United States' Statement of Position pursuant to the preceding Paragraph. The motion shall contain a written statement of the disputing Defendant's position on the matter in dispute, including any supporting factual data, analysis, opinion, or documentation, and shall set forth the relief requested and any schedule within which the dispute must be resolved for orderly implementation of the Consent Decree.

31. The United States shall respond to Defendant's motion within the time period allowed by the Local Rules of this Court. Defendant may file a reply memorandum, to the extent permitted by the Local Rules.

32. Standard of Review. In a formal dispute resolution proceeding under this Section, Defendants shall bear the burden of demonstrating that their position complies with this Consent Decree and the Act. The Court shall decide the dispute based on applicable principles of law. The United States reserves the right to argue that its position is reviewable only on the administrative record and must be upheld unless arbitrary and capricious or otherwise not in accordance with law.

33. The invocation of dispute resolution procedures under this Section shall not, by itself, extend, postpone, or affect in any way any obligation of either Defendant under this Consent Decree, unless and until final resolution of the dispute so provides. Stipulated penalties with respect to the disputed matter shall continue to accrue from the first Day of noncompliance, but payment shall be stayed pending resolution of the dispute as provided in Paragraph 22. If the disputing Defendant does not prevail on the disputed issue, stipulated penalties shall be assessed

and paid by the disputing Defendant as provided in Section VII (Stipulated Penalties).

IX. INFORMATION COLLECTION AND RETENTION

34. The United States, the State, and their representatives, including attorneys, contractors, and consultants, shall have the right of entry into any facility covered by this Consent Decree, at all reasonable times, upon presentation of credentials, to:

- a. monitor the progress of activities required under this Consent Decree;
- b. verify any data or information submitted to the United States or the State in accordance with the terms of this Consent Decree;
- c. obtain samples and, upon request, splits of any samples taken by either Defendant or its representatives, contractors, or consultants;
- d. obtain documentary evidence, including photographs and similar data; and
- e. assess each Defendant's compliance with this Consent Decree.

35. Upon request, each Defendant shall provide EPA and the State or their authorized representatives splits of any samples taken by that Defendant. Upon request, EPA and the State shall provide either Defendant splits of any samples taken by EPA or the State.

36. Until three years after the termination of this Consent Decree, each Defendant shall retain, and shall instruct their contractors and agents to preserve, all non-identical copies of all documents, records, or other information (including documents, records, or other information in electronic form) in their or their contractors' or agents' possession or

control, or that comes into their or their contractors' or agents' possession or control, and that relate in any manner to each Defendant's performance of its obligations under this Consent Decree. This information-retention requirement shall apply regardless of any contrary corporate or institutional policies or procedures. At any time during this information-retention period, upon request by the United States or the State, each Defendant shall provide copies of any documents, records, or other information required to be maintained under this Paragraph.

37. At the conclusion of the information-retention period provided in the preceding Paragraph, each Defendant shall notify the United States and the State at least 90 Days prior to the destruction of any documents, records, or other information subject to the requirements of the preceding Paragraph and, upon request by the United States or the State, each Defendant shall deliver any such documents, records, or other information to EPA or the State. Each Defendant may assert that certain documents, records, or other information are privileged under the attorney-client privilege or any other privilege recognized by federal law. If either Defendant asserts such a privilege, it shall provide the following: (1) the title of the document, record, or information; (2) the date of the document, record, or information; (3) the name and title of each author of the document, record, or information; (4) the name and title of each addressee and recipient; (5) a description of the subject of the document, record, or information; and (6) the privilege asserted by that Defendant. However, no documents, records, or other information created or generated pursuant to the requirements of this Consent Decree shall be withheld on grounds of privilege.

38. Each Defendant may also assert that information required to be provided

under this Section is protected as Confidential Business Information (“CBI”) under 40 C.F.R.

Part 2. As to any information that either Defendant seeks to protect as CBI, that Defendant shall follow the procedures set forth in 40 C.F.R. Part 2 and W. Va. Code State R. Tit. 45 § 31.

39. This Consent Decree in no way limits or affects any right of entry and inspection, or any right to obtain information, held by the United States or the State pursuant to applicable federal or state laws, regulations, or permits, nor does it limit or affect any duty or obligation of either Defendant to maintain documents, records, or other information imposed by applicable federal or state laws, regulations, or permits.

X. EFFECT OF SETTLEMENT/RESERVATION OF RIGHTS

40. This Consent Decree resolves the civil claims of the United States and the State for the violations alleged in the Complaint filed in this action through the date of lodging of the Decree.

41. The United States and the State reserve all legal and equitable remedies available to enforce the provisions of this Consent Decree. This Consent Decree shall not be construed to limit the rights of the United States or the State to obtain penalties or injunctive relief under the Act or implementing regulations, or under other federal or state laws, regulations, or permit conditions, except as expressly specified in the preceding Paragraph. The United States and the State further reserve all legal and equitable remedies to address any imminent and substantial endangerment to the public health or welfare or the environment arising at, or posed by, the Facility, whether related to the violations addressed in this Consent Decree or otherwise.

42. This Consent Decree is not a permit, or a modification of any permit,

under any federal, State, or local laws or regulations. Each Defendant is responsible for achieving and maintaining complete compliance with all applicable federal, State, and local laws, regulations, and permits; and a Defendant's compliance with this Consent Decree shall be no defense to any action commenced pursuant to any such laws, regulations, or permits, except as set forth herein. The United States and the State do not, by their consent to the entry of this Consent Decree, warrant or aver in any manner that either Defendant's compliance with any aspect of this Consent Decree will result in compliance with provisions of the Act, or with any other provisions of federal, State, or local laws, regulations, or permits.

43. This Consent Decree does not limit or affect the rights of either Defendant or of the United States or the State against any third parties, not party to this Consent Decree, nor does it limit the rights of third parties, not party to this Consent Decree, against either Defendant, except as otherwise provided by law.

44. This Consent Decree shall not be construed to create rights in, or grant any cause of action to, any third party not party to this Consent Decree.

XI. COSTS

45. The Parties shall bear their own costs of this action, including attorneys' fees, except that the United States and the State shall be entitled to collect the costs (including attorneys' fees) incurred in any action necessary to enforce this Consent Decree, including an action to collect any portion of the civil penalty or any stipulated penalties due but not paid by Defendants.

XII. NOTICES

46. Unless otherwise specified herein, whenever notifications, submissions, or communications are required by this Consent Decree, they shall be made in writing and addressed as follows:

To the United States:

Chief, Environmental Enforcement Section
Environment and Natural Resources Division
U.S. Department of Justice
Box 7611 Ben Franklin Station
Washington, D.C. 20044-7611
Re: DOJ No. 90-5-2-1-09251

and

Chris Pilla, Branch Chief
Air Enforcement Branch
Air Protection Division,
U.S. Environmental Protection Agency
Region III
1650 Arch Street
Philadelphia, PA 19103-2029

and

Donna L. Mastro, Esq.
U.S. Environmental Protection Agency
Region III (3RC10)
1650 Arch Street
Philadelphia, PA 19103-2029

To the State:

Roland T. Huson, Esq.
Office of Legal Services, West Virginia Department of Environmental Protection
601 57th Street
Charleston, WV 25304

Jesse D. Adkins
Chief of Enforcement
Division of Air Quality
West Virginia Department of Environmental Protection
601 57th Street
Charleston, WV 25304

To Lucite:

Marney Gillmore
Director of Manufacturing
Lucite International, Inc.
2665 Fite Road
Memphis, TN 38127

Lee A. DeHihns, III
Alston & Bird LLP
1201 West Peachtree Street
Atlanta, GA 30309-3424

To DuPont:

Bernard J. Reilly, Esq.
DuPont Legal D-7082A
1007 Market Street
Wilmington, DE 19898

Thomas E. Knauer, Esq.
1011 East Main Street, Suite 310
Richmond, VA 23219

E.I. Du Pont de Nemours and Company
Attn: Director, Sulfuric Acid Business
1007 Market Street
Wilmington, DE 19898

47. Any Party may, by written notice to the other Parties, change its designated notice recipient or notice address provided above.

48. Notices submitted pursuant to this Section shall be deemed submitted

upon mailing, unless otherwise provided in this Consent Decree or by mutual agreement of the Parties in writing.

XIII. EFFECTIVE DATE

49. The Effective Date of this Consent Decree shall be the date upon which this Consent Decree is entered by the Court as recorded on the Court's docket.

XIV. RETENTION OF JURISDICTION

50. The Court shall retain jurisdiction over this case until termination of this Consent Decree, for the purpose of resolving disputes arising under this Decree or entering orders modifying this Decree, pursuant to Sections XV and XVI, or effectuating or enforcing compliance with the terms of this Decree.

XV. MODIFICATION

51. Except as provided in Paragraph 47, the terms of this Consent Decree may be modified only by a subsequent written agreement signed by all the Parties. Where the modification constitutes a material change to this Decree, it shall be effective only upon approval by the Court.

52. Any disputes concerning modification of this Decree shall be resolved pursuant to Section VIII of this Decree (Dispute Resolution), provided, however, that the Party seeking the modification bears the burden of demonstrating that it is entitled to the requested modification in accordance with Federal Rule of Civil Procedure 60(b).

XVI. TERMINATION

53. After Defendants have completed the requirements of Section V

(Compliance Requirements) of this Decree, and have paid the civil penalty and any accrued stipulated penalties as required by this Consent Decree, Defendants may submit to the United States and the State a Joint Request for Termination, stating that Defendants have satisfied those requirements, together with all necessary supporting documentation.

54. Following receipt by the United States and the State of Defendants' Joint Request for Termination, the Parties shall confer informally concerning the Request and any disagreement that the Parties may have as to whether both Defendants have satisfactorily complied with the requirements for termination of this Consent Decree. If the United States, after consultation with the State, agrees that the Decree may be terminated, the Parties shall submit, for the Court's approval, a joint stipulation terminating the Decree.

55. If the United States after consultation with the State does not agree that the Decree may be terminated, either Defendant may invoke Dispute Resolution under Section VIII of this Decree. However, neither Defendant shall seek Dispute Resolution of any dispute regarding termination, until ninety (90) Days after service of its Request for Termination.

XVII. PUBLIC PARTICIPATION

56. This Consent Decree shall be lodged with the Court for a period of not less than thirty (30) Days for public notice and comment in accordance with 28 C.F.R. § 50.7. The United States reserves the right to withdraw or withhold its consent if the comments regarding the Consent Decree disclose facts or considerations indicating that the Consent Decree is inappropriate, improper, or inadequate. Each Defendant consents to entry of this Consent Decree without further notice.

XVIII. SIGNATORIES/SERVICE

57. The undersigned representatives of Defendants, the State of West Virginia, and the Assistant Attorney General for the United States each certify that he or she is duly authorized to enter into the terms and conditions of this Consent Decree and to execute and legally bind the Party he or she represents to the terms of the Decree.

58. This Consent Decree may be signed in counterparts, and its validity shall not be challenged on that basis. Each Defendant agrees to accept service of process by mail with respect to all matters arising under or relating to this Consent Decree and to waive the formal service requirements set forth in Rules 4 and 5 of the Federal Rules of Civil Procedure and any applicable Local Rules of this Court including, but not limited to, service of a summons.

XIX. INTEGRATION

59. This Consent Decree constitutes the final, complete, and exclusive agreement and understanding among the Parties with respect to the settlement embodied in the Decree and supercedes all prior agreements and understandings, whether oral or written, concerning the settlement embodied herein. Except for the Complaint filed by the Plaintiffs, no other document, nor any representation, inducement, agreement, understanding, or promise, constitutes any part of this Decree or the settlement it represents, nor shall it be used in construing the terms of this Decree.

60. Each limit and/or other requirement established by or under this Consent Decree is a separate, independent requirement.

XX. FINAL JUDGMENT

61. Upon approval and entry of this Consent Decree by the Court, this Consent Decree shall constitute a final judgment of the Court as to the United States, the State, and Defendants. The Court finds that there is no just reason for delay and therefore enters this judgment as a final judgment under Fed. R. Civ. P. 54 and 58.

Dated and entered this ____ day of _____, 200__.

UNITED STATES DISTRICT JUDGE
Southern District of West Virginia

THE UNDERSIGNED PARTIES enter into this Consent Decree in the matter of United States, et al., v. E.I. Du Pont Nemours & Co., et al. (S.D. WV), relating to alleged violations of the Clean Air Act:

FOR PLAINTIFF UNITED STATES OF AMERICA:

JOHN C. CRUDEN
Acting Assistant Attorney General
Environment and Natural Resources Division
United States Department of Justice

Date

MARCELLO MOLLO
Trial Attorney
Environmental Enforcement Section
Environment and Natural Resources Division
United States Department of Justice
P.O. Box 7611
Washington, DC 20044
Phone: (202) 514-2757
Facsimile: (202) 616-6583
marcello.mollo@usdoj.gov

Date

CHARLES T. MILLER
United States Attorney
Southern District of West Virginia

s/Kelly R. Curry
KELLY R. CURRY
Assistant United States Attorney
WV State Bar No. 7645
Attorney for United States
P.O. Box 1713, Charleston, WV 25326
Phone: 304-345-2200
Facsimile: 304-347-5443
kelly.curry@usdoj.gov

THE UNDERSIGNED PARTIES enter into this Consent Decree in the matter of United States, et al., v. E.I. Du Pont Nemours & Co., et al. (S.D. WV), relating to alleged violations of the Clean Air Act:

FOR PLAINTIFF EPA REGION III:

WILLIAM T. WISNIEWSKI
Acting Regional Administrator
U.S. EPA Region III
1650 Arch Street
Philadelphia, PA 19103

Date

WILLIAM C. EARLY
Regional Counsel
U.S. EPA Region III
1650 Arch Street
Philadelphia, PA 19103

Date

DONNA L. MASTRO
Senior Assistant Regional Counsel
U.S. EPA Region III
1650 Arch Street
Philadelphia, PA 19103

Date

THE UNDERSIGNED PARTIES enter into this Consent Decree in the matter of United States, et al., v. E.I. Du Pont Nemours & Co., et al. (S.D. WV), relating to alleged violations of the Clean Air Act:

FOR PLAINTIFF THE UNITED STATES ENVIRONMENTAL PROTECTION AGENCY:

CATHERINE MCCABE
Assistant Administrator for
Enforcement and Compliance Assurance
United States Environmental Protection Agency

Date

THE UNDERSIGNED PARTIES enter into this Consent Decree in the matter of United States, et al., v. E.I. Du Pont Nemours & Co., et al. (S.D. WV), relating to alleged violations of the Clean Air Act:

FOR PLAINTIFF STATE OF WEST VIRGINIA:

JOHN A. BENEDICT

Date

Director

Division of Air Quality

West Virginia Department of Environmental Protection

ROLAND T. HUSON, III

Date

Senior Counsel

Office of Legal Services

West Virginia Department of Environmental Protection

THE UNDERSIGNED PARTIES enter into this Consent Decree in the matter of United States, et al., v. E.I. Du Pont Nemours & Co., et al. (S.D. WV), relating to alleged violations of the Clean Air Act:

FOR DEFENDANT E.I. DU PONT DE NEMOURS & CO.:

GARY W. SPITZER
Vice President & General Manager
DuPont Chemical Solutions Enterprise

Date

The following is the name and address of Settling Defendant's agent for service and counsel:

Bernard J. Reilly, Esq.
DuPont Legal D-7082A
1007 Market Street
Wilmington, DE 19898

THE UNDERSIGNED PARTIES enter into this Consent Decree in the matter of United States, et al., v. E.I. Du Pont Nemours & Co., et al. (S.D. WV), relating to alleged violations of the Clean Air Act:

FOR DEFENDANT LUCITE INTERNATIONAL, INC.:

MARNEY GILLMORE
Director of Manufacturing
Lucite International, Inc.
2665 Fite Road
Memphis, TN 38127

Date

The following is the name and address of Settling Defendant's agent for service and counsel:

Lee A. DeHihns, III
Alston & Bird LLP
1201 West Peachtree Street
Atlanta, GA 30309-3424

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF POLLUTION PREVENTION AND TOXICS
REGULATION OF NEW CHEMICAL SUBSTANCES
PENDING DEVELOPMENT OF INFORMATION

RA
3/10/09
4P
3/11/09
TK
4/9/09

In the matter of:

Premanufacture Notice Numbers:

DuPont Company

P-08-508 and P-08-509

EPA SANITIZED

Consent Order and Determinations Supporting Consent Order

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I. INTRODUCTION

Under the authority of § 5(e) of the Toxic Substances Control Act ("TSCA") (15 U.S.C. 2604(e)), the Environmental Protection Agency ("EPA" or "the Agency") issues the attached Order, regarding premanufacture notices ("PMNs") P-08-508 for the chemical substance [] and P-08-509 for the chemical substance []

[] ("the PMN substances") submitted by DuPont Company ("the Company"), to take effect upon expiration of the PMN review period. The Company submitted the PMNs to EPA pursuant to § 5(a)(1) of TSCA and 40 CFR Part 720.

Under § 15 of TSCA, it is unlawful for any person to fail or refuse to comply with any provision of § 5 or any order issued under § 5. Violators may be subject to various penalties and to both criminal and civil liability pursuant to § 16, and to specific enforcement and seizure pursuant to § 17. In addition, chemical substances subject to an Order issued under § 5 of TSCA, such as this one, are subject to the § 12(b) export notice requirement.

II. SUMMARY OF TERMS OF THE ORDER

The Consent Order for these PMN substances requires the Company to:

- (a) submit to EPA certain toxicity and pharmacokinetics testing on the PMN substance described in P-08-509 at least 14 weeks before manufacturing or importing a total of [] kilograms (kgs) of the two PMN substances (or 2 years, whichever comes later, for two of the studies) and [] kgs of the two PMN substances combined;

(b) require any workers who may be exposed to wear impervious gloves and distribute the PMN substances to only those customers that agree to require impervious gloves;

(c) require any workers who may be exposed via inhalation to P-08-508 to wear a respirator with a NIOSH Assigned Protection Factor ("APF") of 3000 and distribute to only those customers that agree to require those respirators;

(d) require any workers who may be exposed via inhalation to P-08-509 to wear an appropriate NIOSH-approved respirator and distribute only to customers that agree to require respirators for any workers reasonably likely to be exposed by inhalation;

(e) as an alternative to using respirators, maintain workplace airborne concentrations of the PMN substances in the United States at or below a specified New Chemical Exposure Limit ("NCEL") of 0.01 mg/m³ (based on the current ACGIH TLV/TWA for the ammonium salt of perfluorooctanoic acid ("APFO")) and distribute only to those customers in the United States that maintain this NCEL. (To pursue this option, a sampling and analytical method must be developed by the Company, verified by an independent third-party laboratory, and submitted to EPA.);

(f) for operations in the United States, recover and capture (destroy) or recycle the PMN substances from all the process wastewater effluent streams and air emissions (point source and fugitive) at an overall efficiency of 99% and distribute only to those customers that achieve this percentage of efficiency or destruction;

(g) distribute the polymers containing the PMN substances (residuals) at levels not to exceed those specified in this Order and verified using the method in Larsen et al. (2006);

and

(h) maintain certain records.

III. CONTENTS OF PMN

Confidential Business Information Claims (Bracketed in the Preamble and Order): specific chemical identity, production volume, manufacturing process and sites, processing, use, and other information

Chemical Identities:

Specific: P-08-508 []

CAS no.: [] and P-08-509 []
[] CAS no.: []

Generic chemical identity: P-08-508- Perfluorinated aliphatic carboxylic acid and P-08-509-Perfluorinated Aliphatic Carboxylic Acid, Ammonium Salt

Use:

Specific: P-08-508-[] and P-08-509-[]
[] Intended to replace []
[]

Generic: P-08-508-Intermediate for polymerization aid, P-08-509-polymerization aid

Maximum 12-Month Production Volume: P-08-508-[] kgs, P-08-509-[] kgs

Test Data Submitted with PMN: Physical and Chemical characteristics; Determination of the Dissociation Constant (salt); Determination of Water Solubility and Vapor Pressure; Biopersistence and Pharmacokinetic Screen in the Rat; In Vitro Trout Hepatocyte

Bioaccumulation Screen; Thermal Decomposition Study results

Toxicity: Acute oral toxicity, up-and-down procedure and Acute Oral Test (rats and mice); Approximate Lethal Dose (ALD) in rats and mice; Acute Dermal Toxicity in Rats; Approximate Lethal Dose (ALD) by Skin Absorption in Rabbits; Local Lymph Node Assay (LLNA) in Mice; Acute Eye Irritation in rabbits; Acute Dermal Irritation Study in Rabbits; 7-day Repeated Dose Oral Toxicity in Rats and Male Mice; 28-Day Repeated Dose Oral Toxicity Study in Rats and Mice; Corrositex in vitro test; Combined Two Week Inhalation Toxicity and Micronucleus Studies in Rats-Transformation Byproduct. In Vitro Micronucleus and Chromosome Aberration Assay in Mouse Bone Marrow Cells; In Vitro Rat Hepatocyte Screen, Bacterial Acute Mutation test; Determination of permeability coefficient (Kp) using a static in vitro diffusion cell model; In Vitro evaluation for Chromosome Aberrations in Human Lymphocytes-transformation byproduct

Mutagenicity test in Salmonella Typhimurium-transformation; byproduct; Combined two week inhalation toxicity and micronucleus studies in -transformation byproduct; Water solubility, vapor pressure, and octanol water partition coefficient and other p-chem properties of transformation byproduct; Thermal Transformation Byproduct

Ecotoxicity/Fate: Acute toxicity to fish (Rainbow trout), daphnia, and algae; Ready Biodegradability Study; Activated Sludge Respiration Inhibition Test; and Assessment of Hydrolysis as a Function of pH

In general, the test substance was the salt (509), except for some acute studies, pharmacokinetics, and mutagenicity where the test substance was both the acid (508) and the salt (509) or as noted below. For a complete listing, see the PMN.

IV. EPA'S ASSESSMENT OF EXPOSURE AND RISK

The following are EPA's predictions regarding the probable toxicity, human exposure and environmental release of the PMN substances, based on the information currently available to the Agency.

Human Health Effects and Fate Summary:

EPA has concerns that these PMN substances will persist in the environment, could bioaccumulate, and be toxic ("PBT") to people, wild mammals, and birds. EPA's concerns are based on data on the PMN substances, analogy to other [] chemicals, and to perfluorooctanoic acid ("PFOA") and perfluorooctane sulfonate ("PFOS") which are both currently under review by EPA for PBT concerns. Some [], PFOA, and PFOS are expected to persist for years in the environment. Biodegradation and photolysis tests of some analogous substances indicate little or no biodegradation or photolysis of perfluoroalkyl compounds. Bioaccumulation concerns are based on the measured presence of certain perfluoroalkyl compounds, including PFOA, in wildlife and in human blood samples.

Based on test data on structurally similar [] chemicals and data on the PMN substances themselves, EPA has human health concerns for the PMN substances. The PMN substances are expected to be absorbed by all routes of exposure. The PMN substances show low acute oral toxicity (≥ 3400 mg/kg). The acute dermal toxicity study with P-08-509 shows low acute dermal toxicity (>5000 mg/kg). The PMN substance P-08-508 is expected to be highly irritating or corrosive. There is high concern for eye irritation for both PMN substances.

The PMN substance P08-509 was tested in a 28-day repeated dose study in rats and mice. In the rat study, the doses were 0, 0.3, 3, and 30 mg/kg/day in males and 0, 3, 30, and 300 mg/kg/day in females. The EPA reviewer set the NOAEL in males at 0.3 mg/kg/day based on dose related trends and statistical significance of change in hematologic findings (decreases in red blood cell counts, hemoglobin, and hematocrit in males), increase in clinical chemistry, increases in absolute and relative organ/body and liver weights. Histopathologic findings in the liver included minimal or mild hepatocellular hypertrophy in males at 3 and 30 mg/kg/day. In this study in rats, the EPA reviewer set the NOAEL at 30 mg/kg/day in females based on increased liver weights and liver pathology as hepatocellular hypertrophy in females given 300 mg/kg/day. The investigators concluded that the NOAELs were 30 mg/kg/day in males and 300 mg/kg/day in females, stating that all changes in treated groups are within historical control ranges at the testing facility and as adaptive responses.

In the mouse study, the doses were 0 (vehicle control), 0.1, 3, or 30 mg/kg/day of test substance in deionized water by gavage daily for 28 days with terminal sacrifice on day 29. In addition, 10 male and female mice were similarly treated with 0 (vehicle control), 30 (males), or 300 (females) mg/kg/day and killed after 28 days of recovery following treatment.

The EPA reviewer set the NOAEL at 0.1 mg/kg/day based on signs of anemia and liver effects at higher dose levels. The investigators placed the NOAEL at 0.1 mg/kg/day in males and 3 in females.

A related [] substance was also tested in a 28-day study in rats. The doses were 0, 5, 25, and 100 mg/kg/day with a NOAEL of 5 mg/kg/day and effects on the liver and kidney at 25 and 100 mg/kg/day. A single dose pharmacokinetic study was conducted in the rat and the

monkey. Male and female results were similar. Toxicity studies on some [] have shown systemic toxicity in animals at levels as low as 0.13 mg/kg in a 90-day oral toxicity study.

Some data exists on the transformation product [] and [] in combined two week inhalation toxicity and micronucleus studies. Doses were 0, 5,000, 25,000 and 175,000 ppm. The NOAEL was determined to be 175,000 ppm. No systemic toxicity relevant to humans was exhibited for []. For [], increased absolute and relative liver weights were seen in this limited study at 25,000 ppm. Mutagenicity in this study was negative.

Several mutagenicity studies were conducted on both PMN substances, P-08-508 and 509. They were not gene mutagens in two species of prokaryotes, and not inducers of DNA effects in mammalian cells *in vivo*. They were chromosome mutagens in mammalian and human cells in culture, but not in mammals *in vivo*. The EPA reviewer concluded that the positive data on the PMNs for *in vitro* chromosomal aberrations in mammalian and human cells are of some concern. However, the negative responses for *in vivo* chromosomal effects as micronuclei and as chromosomal aberrations, and for induction of DNA effects, alleviates that concern. No additional mutagenicity testing is recommended.

For chronic and carcinogenic effects, no information was submitted. EPA believes that a 2-year Chronic Toxicity/Carcinogenicity study (OPPTS 870.3100, OECD 453) is needed.

Pharmacokinetic studies were conducted in rats. Groups of 3 male and 3 female rats were dosed via single oral gavage with either 10 or 30 mg/kg of the PMN substance P-08-508 (98%) and P-08-509 (84.5%). Blood samples were taken before dosing and periodically thereafter up to 168 hours (7 days) after dosing. In addition, fat and liver samples were taken at terminal sacrifice. Samples were analyzed for the parent compound using HPLC/MS with a level of

quantitation (LOQ) at 20 ng/ml. Clearance times were calculated for the 2 doses for males and females as follows:

	10 mg/kg (508)	30 mg/kg (508)	10 mg/kg (509)	30 mg/kg (509)
Male	28 hr	22 hr	12 hr	22 hr
Female	8 hr	4 hr	4 hr	8 hr

The Company has done some limited biomonitoring in workers and site monitoring. EPA has reviewed the biomonitoring and concluded that samples did not take place over a long enough period of time to see if accumulation occurred and that the limit of detection was not sensitive enough to draw any conclusions at this time.

Toxicity studies on the analogs PFOA and PFOS indicate developmental, reproductive and systemic toxicity in various species. Cancer may also be of concern. These factors, taken together, raise concerns for potential adverse chronic effects in humans and wildlife. For additional information about PFOA, consult the docket EPA-HQ -OPPT-2003-0013. Additional information about PFOA and other perfluorinated substances may also be found in the *Administrative Record for PFOS, PFOA, and Telomers and Related Chemicals (AR-226)*. *Administrative Record (AR-226)* is not currently available online, but copies can be requested on CD-ROM from the EPA Docket office by calling 202/566-0280 or sending an email request to oppt.ncic@epa.gov.

The data on the PMN substance and some other data indicate a different and less toxic profile for the PMN substances than for PFOA and PFOS. However, based on: 1) the persistence of the PMN substances, 2) the toxicity of the PMN substances and some of the [] analogs, and 3) the possibility or likelihood that this substance may be used as

a major substitute for a major use of PFOA, EPA believes that more information is needed on the toxicity and pharmacokinetics of the PMN substance P-08-509 that will be applied to the characterization of both PMN substances.

EPA believes that additional pharmacokinetic, reproductive, and long-term toxicological testing on the PMN substance P-08-509 in animals is warranted. EPA will require at a certain production volume that a modified reproductive test (OECD 421, modified) be conducted. The modifications for the reproductive test include: (1) increase the parental sample size to 20; (2) the duration of the study should be extended to until the pups have reached sexual maturation; (3) parental males should be dosed for 10 weeks prior to mating; (4) dosing of the parental animals should be continued through lactation and then the pups should be directly dosed until they reach sexual maturation; (5) pup body weight should be recorded on lactation days 0, 4, 7, 14, and 21 and then at weekly intervals, (6) litter size can be standardized to 4 pups/litter on lactation day 4 (optional); (7) at weaning one pup/sex/litter shall be randomly selected to follow until sexual maturation; and (8) the time of sexual maturation should be recorded (i.e. vaginal opening and preputial separation). In addition, the Company will also conduct Repeated Dose Pharmacokinetics and Metabolism testing (OPPTS 870.7485); a Combined Carcinogenicity/Chronic Toxicity test (OPPTS 870.4300/OECD 453); and an Avian Reproduction test (OECD 206, OPPTS 850.2300).

Environmental Effects Summary:

EPA expects the PMN substances to be highly persistent in the environment. In addition, they may be bio-accumulative or biopersistent based on the predicted log K_{oc} and because some

related substances show evidence of biopersistence. No short-term ecotoxicological concerns were raised for the PMN substances. Reported results in acute toxicity tests in fish (rainbow trout), *Daphnia magna* and green algae were: fish-96 hr LC 50>96.9 mg/l; *Daphnia magna* 48 hr EC50 > 102 mg/l; and 72 hr EC50>106 mg/l. However, there is high concern for possible environmental effects over the long-term. As stated previously, the analog PFOA is persistent in the environment and has a long bioretention time in various species. It has been detected in a number of species of wildlife, including marine mammals. It is toxic to mammalian and other species. The presence in the environment and toxicological properties of PFOA continue to be investigated. EPA believes development of additional data is warranted. EPA will require at a certain production volume that a Fish Early Life Stage Toxicity test (OPPTS 850.1400), a Daphnid Chronic Toxicity test (OPPTS 850.1300), and an Avian Reproduction test-Bobwhite Quail (OPPTS 850.2300) be conducted.

Exposure and Environmental Release Summary:

These PMN substances will be manufactured by [

J. P-08-509 will

be used as a polymerization aid in the manufacture of

[].

Several points of exposure and release were submitted and evaluated for these PMN substances. Doses were calculated for dermal and inhalation exposure to P-08-508 from loading and unloading drums and sampling. Inhalation exposures are to vapors with up to 20 workers potentially exposed. EPA estimates that these quantities could be between 3.8 mg/day (typical) to 230 mg/day (worst case). There may be dermal exposure to a liquid containing P-08-508. For P-08-509, manufacture and use were assumed at up to 3 sites (2 DuPont sites and one potential customer site). According to the Company, only one site will be used at a time. At these sites, the material will be unloaded and charged to various process vessels, such as a blend tank or a polykettle. Due to the low vapor pressure of P-08-509, only dermal exposure was evaluated. Based on the possibility of inadvertent exposure at low levels, the Order requires that any person who is reasonably likely to be exposed by inhalation to the PMN substance P-08-509 to wear an appropriate NIOSH-approved respirator. EPA has established for both PMN substances a New Chemical Exposure Limit ("NCEL") at 0.01 mg/m³, the Threshold Limit Value ("TLV") currently recommended for APFO by the ACGIH in the United States, in order to "level the playing field" and allow the substitution of the PMN substance P-08-509 into the marketplace. EPA believes that this limit should be adequate for the PMN substances based on current information. If this ACGIH level were to change or there is data on the PMN substances that EPA believes warrants a change, the NCEL may be changed in order to correspond with the new level or data.

Releases to the environment were estimated to water and to air (fugitive) and to air via incineration. Based on submitter information, the Company currently collects the waste containing the PMN substances and sends the waste to an off-site RCRA incinerator. In the future, the Company intends to develop and use methods to recapture and/or recycle the substances, but is not now doing so. EPA requires in the attached Consent Order that the substances be recovered, recycled and/or destroyed at levels achieving 99% efficiency. EPA will require that the Company directly sell the substances only to customers, if any, that achieve comparable recovery or destruction. The Company shall distribute the PMN substance, P-08-509 in polymers, aqueous or solid, so that the residual P-08-508/509 cumulative total [

] are below 200 ppb level using the ASE method developed by Larsen et al. (The Analyst 2006 p. 1105) with the level of quantification (LOQ) for the standard solution at 0.5 ppb. If non-heat treated solid polymer is distributed then the substance cannot be further distributed, until it is sufficiently heat treated. The Company should make every effort to minimize or prevent any release to the environment of these substances. If any new uses of the substance are found, the Company shall find ways to recover and/or recycle the substance to comparable levels. Fugitive releases may be of particular concern.

V. EPA'S CONCLUSIONS OF LAW

The following findings constitute the basis of the Consent Order:

A. EPA is unable to determine the potential for human health and environmental effects from exposure to the PMN substances. EPA therefore concludes, pursuant to § 5(e)(1)(A)(i) of TSCA,

that the information available to the Agency is insufficient to permit a reasoned evaluation of the human health and environmental effects of the PMN substances.

B. In light of the potential risk of human health and environmental effects posed by the uncontrolled manufacture, import, processing, distribution in commerce, use, and disposal of the PMN substances, EPA has concluded, pursuant to § 5(e)(1)(A)(ii)(I) of TSCA, that uncontrolled manufacture, import, processing, distribution in commerce, use, and disposal of the PMN substances may present an unreasonable risk of injury to human health and the environment.

C. In light of the estimated production volume of, environmental release of, and human exposure to, the PMN substances, EPA has further concluded, pursuant to § 5(e)(1)(A)(ii)(II) of TSCA, that the PMN substances will be produced in substantial quantities for a potential PBT substance, may reasonably be anticipated to enter the environment in substantial quantities for a potential PBT substance, and there may be significant (or substantial) human exposure to the substances.

VI. INFORMATION REQUIRED TO EVALUATE HUMAN HEALTH AND ENVIRONMENTAL EFFECTS

Triggered Testing. The Order prohibits the Company from exceeding specified production volumes unless the Company submits the information described in the Testing section of this Order in accordance with the conditions specified in the Testing section.

Pended Testing. The Order does not require submission of the following information at any specified time or production volume. However, the Order's restrictions on manufacture, import, processing, distribution in commerce, use, and disposal of the PMN substances will

remain in effect until the Order is modified or revoked by EPA based on submission of the following or other relevant information.

Fate and Physical/Chemical Properties information as follows:

Physical/Chemical Property Testing	OPPTS or OECD Guideline
UV visible absorption	OPPTS 830.7050 or OECD 101
Hydrolysis as a function of pH	OPPTS 835.2130 or OECD 111

Environmental Fate Testing	OPPTS or OECD Guideline
Modified Semi-Continuous Activated Sludge (SCAS) with Analysis for degradation products	OPPTS 835.5045, OPPTS 835.3210 or OECD 302A
Aerobic and Anaerobic Transformation in Soil	OECD 307
Aerobic and Anaerobic transformations in Aquatic Sediment Systems	OECD 308
Direct Photolysis in Water (if wavelengths >290 nm are absorbed)	OPPTS 835.2210
Indirect Photolysis in Water	OPPTS 835.5270
Phototransformation of Chemicals on Soil Surfaces	OECD Jan. 2002 Draft
Simulation test-Aerobic Sewage Treatment (Activated Sludge Units)	OECD 303A
Anaerobic biodegradability of organic compounds in digested sludge	OECD 311
Fish Bioconcentration test	OPPTS 850.1730

CONSENT ORDER

I. SCOPE OF APPLICABILITY AND EXEMPTIONS

(a) **Scope.** The requirements of this Order apply to all commercial manufacturing, processing, distribution in commerce, use and disposal of the chemical substances [

] (P-08-508) and [

] (P-08-509) ("the PMN substances")

in the United States by DuPont Company ("the Company"), except to the extent that those activities are exempted by paragraph (b).

(b) **Exemptions.** Manufacturing, processing, distribution in commerce, use and disposal of the PMN substances is exempt from the requirements of this Order (except the requirements in the Recordkeeping and Successor Liability Upon Transfer Of Consent Order sections) only to the extent that (1) these activities are conducted in full compliance with all applicable requirements of the following exemptions, and (2) such compliance is documented by appropriate recordkeeping as required in the Recordkeeping section of this Order.

(1) **Export.** Until the Company begins commercial manufacture of the PMN substances

for use in the United States, the requirements of this Order do not apply to manufacture, processing or distribution in commerce of the PMN substances solely for export in accordance with TSCA §12(a) and (b), 40 CFR 720.3(s) and 40 CFR Part 707. However, once the Company begins to manufacture the PMN substances for use in the United States, no further activity by the Company involving the PMN substances is exempt as “solely for export” even if some amount of the PMN substances is later exported. At that point, the requirements of this Order apply to all activities associated with the PMN substances while in the territory of the United States. Prior to leaving U.S. territory, even those quantities or batches of the PMN substances that are destined for export are subject to terms of the Order, and count towards any production volume test triggers in the Testing section of this Order.

(2) Research & Development (“R&D”). The requirements of this Order do not apply to manufacturing, processing, distribution in commerce, use and disposal of the PMN substances in small quantities solely for research and development in accordance with TSCA §5(h)(3), 40 CFR 720.3(cc), and 40 CFR 720.36. The requirements of this Order also do not apply to manufacturing, processing, distribution in commerce, use and disposal of the PMN substances when manufactured solely for non-commercial research and development per 40 CFR 720.30(i) and TSCA §5(i).

(3) Byproducts. The requirements of this Order do not apply to the PMN substances when they are produced, without separate commercial intent, only as a “byproduct” as defined at 40 CFR 720.3(d) and in compliance with 40 CFR 720.30(g).

(4) No Separate Commercial Purpose. The requirements of this Order do not apply to the PMN substances when they are manufactured, pursuant to any of the exemptions in 40 CFR

720.30(h), with no commercial purpose separate from the substance, mixture, or article of which it is a part.

(5) Imported Articles. The requirements of this Order do not apply to the PMN substances when they are imported as part of an "article" as defined at 40 CFR 720.3(c) and in compliance with 40 CFR 720.22(b)(1).

(c) Automatic Sunset. If the Company has obtained for the PMN substances a Test Market Exemption ("TME") under TSCA §5(h)(1) and 40 CFR 720.38 or a Low Volume Exemption ("LVE") or Low Release and Exposure Exemption ("LoREX") under TSCA §5(h)(4) and 40 CFR 723.50(c)(1) and (2) respectively, any such exemption is automatically rendered null and void as of the effective date of this Consent Order.

**II. TERMS OF MANUFACTURE, IMPORT, PROCESSING,
DISTRIBUTION IN COMMERCE, USE, AND DISPOSAL
PENDING SUBMISSION AND EVALUATION OF INFORMATION**

PROHIBITION

The Company is prohibited from manufacturing, importing, processing, distributing in commerce, using, or disposing of the PMN substances in the United States, for any nonexempt commercial purpose, pending the development of information necessary for a reasoned evaluation of the human health and environmental effects of the substance, and the completion of EPA's review of, and regulatory action based on, that information, except in accordance with the conditions described in this Order.

TESTING

(a) **Section 8(e) Reporting.** Any information on the PMN substances which reasonably supports the conclusion that the PMN substances presents a substantial risk of injury to health or the environment required to be reported under EPA's section 8(e) policy statement at 43 Federal Register 11110 (March 16, 1978) as amended at 52 Federal Register 20083 (May 29, 1987), shall reference the appropriate PMN identification number for this substance and shall contain a statement that the substance is subject to this Consent Order. Additional information regarding section 8(e) reporting requirements can be found in the reporting guide referenced at 56 Federal Register 28458 (June 20, 1991).

(b) **Notice of Study Scheduling.** The Company shall notify, in writing, the EPA Laboratory Data Integrity Branch (2225A), Office of Enforcement and Compliance Assurance, U.S. Environmental Protection Agency, 1200 Pennsylvania Avenue, N.W., Washington, D.C. 20460, of the following information within 10 days of scheduling any study required to be performed pursuant to this Order, or within 15 days after the effective date of this Order, whichever is later:

- (1) The date when the study is scheduled to commence;
- (2) The name and address of the laboratory which will conduct the study;
- (3) The name and telephone number of a person at the Company or the laboratory whom EPA may contact regarding the study; and
- (4) The appropriate PMN identification number for each substance and a statement that the substance is subject to this Consent Order.

(c) Good Laboratory Practice Standards and Test Protocols. Each study required to be performed pursuant to this Order must be conducted according to TSCA Good Laboratory Practice Standards at 40 CFR Part 792 and using methodologies generally accepted in the relevant scientific community at the time the study is initiated. Before starting to conduct any such study, the Company must obtain approval of test protocols from EPA by submitting written protocols. EPA will respond to the Company within 4 weeks of receiving the written protocols. Published test guidelines specified in paragraph (d) provide general guidance for development of test protocols, but are not themselves acceptable protocols. Approval of the test protocol does not mean pre-acceptance of test results. Because the Chronic Daphnid Toxicity study and the 90-day toxicity study enumerated below were begun before the execution of this Order the requirement for submission and approval of the protocols for these two studies only is waived.

(d) Triggered Testing Requirements. (i) The Company is prohibited from manufacturing or importing the PMN substances beyond the following aggregate manufacture and import volumes of both PMN substances combined ("the production limits"), unless the Company conducts the following studies and submits all final reports and underlying data in accordance with the conditions specified in this Testing section.

<u>Production Limit</u>	<u>Study</u>	<u>Guideline</u>
[] kilograms *	1) Repeated dose Metabolism and Pharmacokinetics rats and mice	OPPTS 870.7485
	2) Modified 1-generation Reproduction study	OECD 421, modified, per (iv) below

3) Avian Reproduction-Bobwhite Quail OPPTS 850.2300

4) Fish Early Life Stage Toxicity OPPTS 850.1400

5) Daphnid Chronic Toxicity OPPTS 850.1300

*An alternate Production Limit for studies 1 and 2 only is two years from the date of commencement of nonexempt commercial manufacture of either PMN substance, or [] kilograms, whichever comes later.

[] kilograms 6) 90-day toxicity study OPPTS 870.3100 (OECD 408)

7) Chronic toxicity/
carcinogenicity study OPPTS 870.4300 (OECD 453)

(ii) the test substance shall be the substance described in P-08-509;

(iii) EPA recommends that the Company conduct the pharmacokinetics testing first to confirm species acceptability and to provide a reliable half-life for these substances;

(iv) The modifications for the 1-generation reproduction study (study 2 above) are: 1) increase the parental sample size to 20; 2) the duration of the study shall be extended to until the pups have reached sexual maturation; 3) parental males shall be dosed for 10 weeks prior to mating; 4) dosing of the parental animals shall be continued through lactation and then the pups should be directly dosed until they reach sexual maturation; 5) pup body weight shall be recorded on lactation days 0, 4, 7, 14, and 21 and then at weekly intervals; 6) litter size can be

standardized to 4 pups/litter on lactation day 4 (optional); 7) at weaning one pup/sex/litter shall be randomly selected to follow until sexual maturation; and 8) the time of sexual maturation shall be recorded (i.e. vaginal opening and preputial separation).

(e) Test Reports. The Company shall: (1) conduct each study in good faith, with due care, and in a scientifically valid manner; (2) promptly furnish to EPA the results of any interim phase of each study; and (3) submit, in triplicate (with an additional sanitized copy, if confidential business information is involved), the final report of each study and all underlying data ("the report and data") to EPA no later than 14 weeks prior to exceeding the applicable production limit. The final report shall contain the contents specified in 40 CFR 792.185. Underlying data shall be submitted to EPA in accordance with the applicable "Reporting", "Data and Reporting", and "Test Report" subparagraphs in the applicable test guidelines. However, for purposes of this Consent Order, the word "should" in those subparagraphs shall be interpreted to mean "shall" to make clear that the submission of such information is mandatory. EPA will not require the submission of raw data such as slides and laboratory notebooks unless if EPA finds, on the basis of professional judgment, that an adequate evaluation of the study cannot take place in the absence of these items.

(f) Testing Waivers. The Company is not required to conduct a study specified in paragraph (d) of this Testing section if notified in writing by EPA that it is unnecessary to conduct that study.

(g) Equivocal Data. If EPA finds that the data generated by a study are scientifically equivocal,

the Company may continue to manufacture and import the PMN substances beyond the applicable production limit. To seek relief from any other restrictions of this Order, the Company may make a second attempt to obtain unequivocal data by reconducting the study under the conditions specified in paragraphs (b), (c), and (e)(1) and (2). The testing requirements may be modified, as necessary to permit a reasoned evaluation of the risks presented by the PMN substances, only by mutual consent of EPA and the Company.

(h) EPA Determination of Invalid Data.

(1) Except as described in subparagraph (h)(2), if, within 6 weeks of EPA's receipt of a test report and data, the Company receives written notice that EPA finds that the data generated by a study are scientifically invalid, the Company is prohibited from further manufacture and import of the PMN substances beyond the applicable production limit.

(2) The Company may continue to manufacture and import the PMN substances beyond the applicable production limit only if so notified, in writing, by EPA in response to the Company's compliance with either of the following subparagraphs (h)(2)(i) or (h)(2)(ii).

(i) The Company may reconduct the study in compliance with paragraphs (b), (c), and (e)(1) and (2). If there is sufficient time to reconduct the study and submit the report and data to EPA at least 14 weeks before exceeding the production limit as required by subparagraph (e)(3), the Company shall comply with subparagraph (e)(3). If there is insufficient time for the Company to comply with subparagraph (e)(3), the Company may exceed the production limit and shall submit the report and data in triplicate to EPA within a reasonable period of time, all as specified by EPA in the notice described in subparagraph (h)(1). EPA will respond to the

Company, in writing, within 6 weeks of receiving the Company's report and data.

(ii) The Company may, within 4 weeks of receiving from EPA the notice described in subparagraph (h)(1), submit to EPA a written report refuting EPA's finding. EPA will respond to the Company, in writing, within 4 weeks of receiving the Company's report.

(i) Company Determination of Invalid Data.

(1) Except as described in subparagraph (i)(2), if the Company becomes aware that circumstances clearly beyond the control of the Company or laboratory will prevent, or have prevented, development of scientifically valid data under the conditions specified in paragraphs (c) and (e), the Company remains prohibited from further manufacture and import of the PMN substances beyond the applicable production limit.

(2) The Company may submit to EPA, within 2 weeks of first becoming aware of such circumstances, a written statement explaining why circumstances clearly beyond the control of the Company or laboratory will cause or have caused development of scientifically invalid data. EPA will notify the Company of its response, in writing, within 4 weeks of receiving the Company's report. EPA's written response may either:

(i) allow the Company to continue to manufacture and import the PMN substances beyond the applicable production limit, or

(ii) require the Company to continue to conduct, or to reconduct, the study in compliance with paragraphs (b), (c), and (e)(1) and (2). If there is sufficient time to conduct or reconduct the study and submit the report and data to EPA at least 14 weeks before exceeding the production limit as required by subparagraph (e)(3), the Company shall comply with

subparagraph (e)(3). If there is insufficient time for the Company to comply with subparagraph (e)(3), the Company may exceed the production limit and shall submit the report and data in triplicate to EPA within a reasonable period of time, all as specified by EPA in the notice described in subparagraph (i)(2). EPA will respond to the Company, in writing, within 6 weeks of receiving the Company's report and data, as to whether the Company may continue to manufacture and import beyond the applicable production limit.

(j) Unreasonable Risk.

(1) EPA may notify the Company in writing that EPA finds that the data generated by a study are scientifically valid and unequivocal and indicate that, despite the terms of this Order, the PMN substances will or may present an unreasonable risk of injury to human health or the environment. EPA's notice may specify that the Company undertake certain actions concerning further testing, manufacture, import, processing, distribution, use and/or disposal of the PMN substances to mitigate exposures to or to better characterize the risks presented by the PMN substances. Within 2 weeks from receipt of such a notice, the Company must cease all manufacture, import, processing, distribution, use and disposal of the PMN substances, unless either:

(2) within 2 weeks from receipt of the notice described in subparagraph (j)(1), the Company complies with such requirements as EPA's notice specifies; or

(3) within 4 weeks from receipt of the notice described in subparagraph (j)(1), the Company submits to EPA a written report refuting EPA's finding and/or the appropriateness of any additional requirements imposed by EPA. The Company may continue to manufacture,

import, process, distribute, use and dispose of the PMN substances in accordance with the terms of this Order pending EPA's response to the Company's written report. EPA will respond to the Company, in writing, within 4 weeks of receiving the Company's report. Within 2 weeks of receipt of EPA's written response, the Company shall comply with any requirements imposed by EPA's response or cease all manufacture, import, processing, distribution, use and disposal of the PMN substances.

(k) Other Requirements. Regardless of the satisfaction of any other conditions in this Testing section, the Company must continue to obey all the terms of this Consent Order until otherwise notified in writing by EPA. The Company may, based upon submitted test data or other relevant information, petition EPA to modify or revoke provisions of this Consent Order pursuant to Part VI. of this Consent Order.

PROTECTION IN THE WORKPLACE

(a) Establishment of Program. During manufacturing, processing, and use of the PMN substances at any site controlled by the Company (including any associated packaging and storage and during any cleaning or maintenance of equipment associated with the PMN substances), the Company must establish a program whereby:

(1) General Dermal Protection. Each person who is reasonably likely to be dermally exposed in the work area to the PMN substances through direct handling of the substance or through contact with equipment on which the substance may exist, or because the substance

becomes airborne in a form listed in subparagraph (a)(5) of this section, is provided with, and is required to wear, personal protective equipment that provides a barrier to prevent dermal exposure to the substance in the specific work area where it is selected for use. Each such item of personal protective equipment must be selected and used in accordance with Occupational Safety and Health Administration ("OSHA") dermal protection requirements at 29 CFR 1910.132, 1910.133, and 1910.138.

(2) Specific Dermal Protective Equipment. The dermal personal protective equipment required by subparagraph (a)(1) of this section must include, but is not limited to, the following items:

- (i) Gloves.
- (ii) Full body chemical protective clothing.
- (iii) Chemical goggles or equivalent eye protection.
- (iv) Clothing which covers any other exposed areas of the arms, legs and torso.

Clothing in this subparagraph (a)(2)(iv) need not be tested or evaluated under the requirements of subparagraph (a)(3)

(3) Demonstration of Imperviousness. The Company is able to demonstrate that each item of chemical protective clothing selected, including gloves, provides an impervious barrier to prevent dermal exposure during normal and expected duration and conditions of exposure within the work area by any one or a combination of the following:

(i) Permeation Testing. Testing the material used to make the chemical protective clothing and the construction of the clothing to establish that the protective clothing will be impervious for the expected duration and conditions of exposure. The testing must subject the

chemical protective clothing to the expected conditions of exposure, including the likely combinations of chemical substances to which the clothing may be exposed in the work area. Permeation testing shall be conducted according to the American Society for Testing and Materials ("ASTM") F739 "Standard Test Method for Resistance of Protective Clothing materials to Permeation by Liquids or Gases." Results shall be recorded as a cumulative permeation rate as a function of time (or versus time), and shall be documented in accordance with ASTM F739 using the format specified in ASTM F1194-99 "Guide for Documenting the Results of Chemical Permeation Testing on Protective Clothing Materials." Gloves may not be used for a time period longer than they are actually tested and must be replaced at the end of each work shift during which they are exposed to the PMN substances.

(ii) Manufacturer's Specifications. Evaluating the specifications from the manufacturer or supplier of the chemical protective clothing, or of the material used in construction of the clothing, to establish that the chemical protective clothing will be impervious to the PMN substances alone and in likely combination with other chemical substances in the work area.

(4) Respiratory Protection. Each person who is reasonably likely to be exposed by inhalation in the work area to the PMN substance, P-08-508, in the form listed in subparagraph (a)(5) of this section, is provided with, and is required to wear, at a minimum, a NIOSH-certified respirator with an Applied Protection Factor ("APF") of 3000 from the respirators listed in subparagraph (a)(6) of this section. All respirators must be used in accordance with OSHA and NIOSH respiratory protection requirements at 29 CFR 1910.134 and 42 CFR Part 84. All respirators must be issued, used, and maintained according to an appropriate respiratory

protection program under the OSHA requirements in 29 CFR 1910.134.

In addition, each person who is reasonably likely to be exposed by inhalation in the work area to the PMN substance P-08-509 must be provided with and wear an appropriate NIOSH-approved respirator.

(5) Physical States. The following physical states of airborne chemical substances are listed for subparagraphs (a)(1) and (4) of this section:

- (i) Particulate (including solids or liquid droplets),
- (ii) Gas/vapor (all substances in the gas form), or
- (iii) Combination Gas/Vapor and Particulate (gas and liquid/solid physical states are both present; a good example is paint spray mist, which contains both liquid droplets and vapor).

(6) Authorized Respirators. The following NIOSH-certified respirators meet the minimum requirements for P-08-508 in subparagraph (a)(4) of this section:

- a NIOSH-certified supplied-air respirator operated in pressure demand or other positive pressure mode and equipped with a tight-fitting full face piece.

NEW CHEMICAL EXPOSURE LIMIT

(a) Alternative to Requirements of Respirator Section.

(1) EPA recommends and encourages the use of pollution prevention, source reduction, engineering controls and work practices, rather than respirators, as a means of controlling inhalation exposures whenever practicable.

(2) Whenever a person is reasonably likely to be exposed to the PMN substances by

inhalation, as an alternative to compliance with the respirator requirements in the Protection in the Workplace section of this Order, the Company may comply with the requirements of this New Chemical Exposure Limit section. However, before the Company may deviate from the respirator requirements in the Protection in the Workplace section of this Order, the Company must:

(i) submit to EPA a copy of the Company's sampling and analytical method for the PMN substances, verified in accordance with subsection (c)(3) of this New Chemical Exposure Limit section;

(ii) obtain exposure monitoring results in accordance with this New Chemical Exposure Limit section; and

(iii) based on those exposure monitoring results, select, provide, and ensure use if necessary of the appropriate respiratory protection specified in paragraph (e)(2) of this New Chemical Exposure Limit section by persons who are reasonably likely to be exposed to the PMN substances by inhalation.

(3) After appropriate respiratory protection has been selected at a workplace based on the results of actual exposure monitoring conducted in accordance with this New Chemical Exposure Limit section, the Company shall not, at that workplace, use the respiratory protection required in the Protection in the Workplace section of this Order (unless it is the same as required by this New Chemical Exposure Limit section).

(b) Exposure Limit.

(1) General. The following new chemical exposure limit ("NCEL") for the PMN

substances is an interim level determined by EPA based on the limited information available to the Agency at the time of development of this Order. The NCEL for the PMN substances is as follows:

(i) Time-Weighted Average ("TWA") Limit. The Company shall ensure that no person is exposed to an airborne concentration of both PMN substances combined in excess of 0.01 mg/m³ (the NCEL) as an 8-hour time-weighted average, without using a respirator in accordance with subsection (e) of this New Chemical Exposure Limit section.

(ii) Non-8-Hour Work-shifts. For non-8-hour work-shifts, the NCEL for that work-shift ("NCEL_n") shall be determined by the following equation: $NCEL_n = NCEL \times (8/n) \times [(24-n)/16]$, where n = the number of hours in the actual work-shift.

(2) Automatic Sunset. If, subsequent to the effective date of this Order, OSHA promulgates, pursuant to §6 of the Occupational Safety and Health Act, 29 U.S.C. 655, a final chemical-specific permissible exposure limit ("PEL") specifically applicable to these PMN substances and the OSHA PEL is not challenged in court within 60 days of its promulgation, then any respirator requirements in the Protection in the Workplace section of this Order and any requirements of this New Chemical Exposure Limit section applicable to workers and situations subject to the OSHA PEL shall automatically become null and void. However, the requirements of this Consent Order are not negated by any pre-existing OSHA PEL applicable to the PMN substances.

(c) Performance-Criteria for Sampling and Analytical Method.

(1) Applicability. For initial development and validation of the sampling and analytical

method for the PMN substances, all the requirements of this subsection (c) apply. For subsequent exposure monitoring conducted pursuant to subsection (d) of this New Chemical Exposure Limit section, only the following requirements apply: (c)(4)(i), (4)(ii), (4)(iv)(II), (4)(v)(II), (8), (9), and (10). Any deviation from the requirements of this subsection (c) must be approved in writing by EPA.

(2) Submission of Verified Method and Certification Statement. The Company shall submit to EPA a copy of a validated sampling and analytical method for the PMN substances which satisfies the criteria specified in this subsection (c). The method description shall expressly state how the method compares with each quantitative requirement specified in this subsection (c). The submission must include a written statement, signed by authorized officials of both the Company and the Laboratory, certifying the truth and accuracy of the independent laboratory verification conducted pursuant to subsection (c)(3). To assist EPA in identifying the document, it shall state in a conspicuous, underlined subject-line at the top of the first page: "NCEL Sampling and Analytical Method for PMN # _____," after which the correct PMN number for this chemical substance shall be stated.

(3) Verification of Analytical Method by Independent Third-Party Laboratory.

(i) Verification. The Company shall have an independent reference laboratory ("Laboratory") verify the validity of the analytical method for the PMN substances, in accordance with the other requirements in this subsection (c)(3). It is the Company's responsibility to ensure that the Laboratory complies with all the requirements specified in this subsection (c)(3).

(ii) Independent Reference Laboratory. The independent reference laboratory must be a separate and distinct person (as defined at 40 CFR 720.3(x)) from the Company and

from any other person who may have developed the method for the Company.

(iii) Accreditation. The Laboratory must be accredited by a formally recognized government or private laboratory accreditation program for chemical testing and/or analysis.

(iv) Good Laboratory Practice Standards. The Laboratory verification of the analytical method for the PMN substances must comply with TSCA Good Laboratory Practice Standards ("GLPS") at 40 CFR Part 792. (Certain provisions of the TSCA GLPS applicable to toxicity testing in laboratory animals, such as 40 CFR 792.43 ("Test system care facilities"), 792.45 ("Test system supply facilities") and 792.90 ("Animal and other test system care"), are clearly inapplicable to the NCEL requirements.) However, compliance with TSCA GLPS is not required under this New Chemical Exposure Limit section where the analytical method is verified by a laboratory accredited by either: (A) the American Industrial Hygiene Association ("AIHA") Industrial Hygiene Laboratory Accreditation Program ("IHLAP"); or (B) another comparable program approved in advance in writing by EPA.

(v) Analysis of Duplicate Samples. The Company shall collect six duplicate samples (a total of 12) at the TWA concentration. The samples shall be taken either from a controlled environment (e.g., a sealed chamber or "glove box") which closely resembles the actual workplace conditions or, for solids and liquids with very low vapor pressure, by injecting the PMN substances onto a sample collection device. The duplicate samples shall be collected on identical collection media, at the same time, and under the same conditions. One set of six samples shall immediately be analyzed by the Company, the other set of six samples shall be analyzed by the Laboratory using the method developed by or for the Company.

(vi) Sample Storage Study. If the results of the analysis of duplicate samples

pursuant to paragraph (c)(3)(v) do not satisfy the requirements in paragraph (c)(3)(vii), the Company must perform a sample storage study as follows:

(I) Triplicate Samples. The Company shall collect six triplicate samples (a total of 18) at the TWA concentration. The samples shall be taken either from a controlled environment (e.g., a sealed chamber or "glove box") which closely resembles the actual workplace conditions or, for solids and liquids with very low vapor pressure, by injecting the PMN substances onto a sample collection device. The triplicate samples shall be collected on identical collection media, at the same time, and under the same conditions. One set of six samples shall immediately be analyzed by the Company.

(II) Analysis After Sample Storage. A sample storage evaluation shall be performed with the two remaining sets of six samples. One set of six samples shall be analyzed by the Laboratory using the method developed by or for the Company, and the other shall be analyzed by the Company on the same day as the Laboratory analyzes its six samples. Specialized storage conditions for the samples including extraction conditions, time from sampling to extraction, time from collection or extraction (if applicable) to analysis and storage conditions must be specified in the method description.

(vii) Comparison of Results. The difference between the results of the two sets of six samples analyzed by the Laboratory and the Company as required in either paragraph (c)(3)(v) or (c)(3)(vi)(II) shall be evaluated using a two-sample t-test with unequal variances, and the two sides of the critical regions shall not exceed a 5% significance level. (See Attachment B - Statistical Analysis of NCELS Analytical Method Verification Results.) The arithmetic mean of each set of six samples must be within 10% of the overall arithmetic mean of the two sets of

sample measurements. If the arithmetic mean of each set of six samples is not within 10% of the overall arithmetic mean, then the sample storage time between collection and analysis must be reduced until the average of each set of six samples is within 10% of the overall arithmetic mean.

(4) Accuracy. The sampling and analytical method must clearly demonstrate the following:

(i) General. The sampling and analytical method, and all exposure monitoring data relied on by the Company, shall be accurate to within $\pm 25\%$ at a 95% confidence level for concentrations of the PMN substances ranging from one half the NCEL to twice the NCEL.

(ii) NCEL Quantitation Limits. The analytical method should be capable of reliably quantifying the PMN substances across the full range of reasonably likely exposures. At a minimum, the analytical method must be capable of reliably quantifying from a lower quantitation limit ("LQL") of one half the NCEL to an upper quantitation limit ("UQL") of at least twice the NCEL. If the Company obtains an exposure monitoring sample that is more than 10% above the actual UQL of the analytical method, the Company must comply with paragraph (e)(4)(i).

(iii) Lower Quantitation Limit Signal-To-Noise Ratio. The analytical method shall be capable of quantifying the PMN to a concentration of one half the NCEL with a signal that is at least five times the baseline noise level. Baseline noise must be amplified to a measurable level when possible, even if the required amplification is beyond that used in routine analysis of samples. (If baseline noise cannot be obtained, another reference must be selected. This may be a peak considered to be noise caused by the reagent matrix.) The sampling preparation method must be specified and the detection limit for the analytical procedure must be

reported as mass per injection for chromatographic techniques.

(iv) Instrument Calibration.

(I) Initial Calibration. For method development and validation (but not subsequent exposure monitoring), the initial calibration shall at a minimum consist of five (5) calibration standards with a linear correlation of 0.95 – these five (5) calibration standards must consist of one standard at each of the following concentrations: one half the NCEL ($0.5 \times$ NCEL); between one half and one times the NCEL ($0.5 \times \text{NCEL} < 1 \times \text{NCEL}$); one times the NCEL ($1 \times \text{NCEL}$); between one and two times the NCEL ($1 \times \text{NCEL} < 2 \times \text{NCEL}$), and twice the NCEL ($2 \times \text{NCEL}$).

(II) Continuing Calibration. During each week of both method development/validation and subsequent exposure monitoring, the Company shall conduct both an initial instrument calibration and a continuing calibration. The Company shall perform at least one continuing calibration sample at the NCEL concentration, and at least one additional calibration sample per every 10 samples analyzed. The continuing calibration sample shall fall within $\pm 25\%$ of the initial calibration value. If not, then the initial calibration must be repeated, and any samples associated with that outlying calibration check must be re-analyzed.

(v) Calculated Percent Recovery.

(I) Initial Calculation. For method development and validation, the Company must calculate the percent of the PMN substances recovered by the analytical method from a sample containing a known quantity of the PMN substances. The sample shall be taken either from a controlled environment (e.g., a sealed chamber or "glove box") which closely resembles the actual workplace conditions or, for solids and liquids with very low vapor

pressure, by injecting the PMN substances onto a sample collection device. (Such a sample is referred to as a "matrix spike"). The calculated percent recovery for each matrix spike shall be greater than or equal to 75% and less than or equal to 125%. Spike concentrations for the PMN substances must be included in the sampling and analytical method submitted to EPA.

(II) Subsequent Calculation. During each subsequent exposure monitoring episode or campaign, at least 1 matrix spike, prepared by injecting the PMN substances onto a sample collection device, shall be analyzed. (This matrix spike must be prepared at the NCEL concentration.)

(vi) Sampling Device Capacity. The capacity of the sampling device must be tested and results reported to show under a known and well-defined set of conditions that the device is capable of collecting the new chemical in solid, liquid or vapor phase with minimal loss. The sampling device's capacity (air volume and collected analyte mass) must be specified. For methods that use adsorbent tubes as the collection medium, evidence of the capacity must be provided in the form of breakthrough testing. This testing must be done at a concentration twice the NCEL and under conditions similar to those expected in the workplace. Breakthrough is defined to have occurred when the concentration of the PMN substances in the effluent stream is equal to 5% of the concentration of the influent stream, or when 20% of the PMN substances is detected in the backup section of the sampler.

(vii) Sampling Device Desorption Efficiency. Where applicable, the desorption efficiency must be evaluated for the air sampling device. A minimum of six air samples spiked with the PMN substances at least the NCEL concentration must be prepared. A recovery of at least 75% must be obtained for each of the six samples.

(5) Precision. The estimate of the coefficient of variation of each set of six samples from the controlled atmosphere test (spiked at 1.0 NCEL, per paragraphs (c)(3)(v) or (vi)) must be less than 0.105, including allowance of 0.05 for error due to sampling.

(6) Interpretation of Accuracy and Precision Data.

(i) If a single matrix spike recovery is less than 75% recovery or greater than 125% or the estimated coefficient of variation is greater than 0.105, then the Company must re-prepare the matrix spike, re-sample, and re-analyze all samples associated with such matrix spike or triplicate samples.

(ii) For percent recoveries less than 90% but greater than 75%, correction for low recovery is required. Correct for recovery first by dividing the observed amount by the proportion recovered before determining if measurements fall below the NCEL. For example, if the observed level is 30 mg/m^3 and the percent recovery is 75%, use the value $30 \text{ mg/m}^3 / (0.75) = 40 \text{ mg/m}^3$ when determining whether the levels are below the exposure limit.

(7) Representativeness. All sample conditions used to develop the methodology shall mimic the actual workplace environment expected to be monitored. Conditions such as the temperature, humidity, lighting, and presence of other chemicals, etc. must mimic the conditions in the workplace to be monitored.

(8) Changes Affecting Validity. If the workplace environment changes from the initial conditions described in the verified sampling and analytical method in a way reasonably likely to invalidate the accuracy of the method, then the Company must comply with the respirator requirements in the Protection in the Workplace section of this Order, unless the Company re-validates the method to confirm that the requirements for accuracy and precision in paragraphs

(c)(4) and (5) are met. Examples of possible changes include but are not limited to: introduction of a new chemical substance to the workplace which may interfere with the analysis of the new chemical; introduction of light to the workplace which may interfere with light-sensitive PMN substances; or introduction of water/increased humidity to the workplace which could react with the PMN substances and cause difficulties in collection and analysis.

(9) Comparability. All data and results shall be reported in the same units of measurement as the NCEL.

(10) Responsibility for Method Validity. The independent laboratory verification and EPA receipt of the sampling and analytical method pursuant to this subsection (c) do not ensure that the method will produce valid exposure monitoring data. The Company is ultimately responsible for ensuring the validity of its exposure monitoring data.

(d) Monitoring Potential Exposure.

(1) General.

(i) Action Level. The "action level" is defined as an airborne concentration of the PMN substances, calculated as an 8-hour time-weighted average, equal to one half the NCEL TWA specified in subparagraph (b)(1). For non-8-hour work shifts, the action level is equal to one half the NCEL_n. (The NCEL_n is described in subparagraph (b)(1)(ii).) The Company may exceed the action level without penalty. The purpose of the action level is solely to determine the requisite monitoring frequency.

(ii) Representative Exposure Groups. Whenever exposure monitoring is required by this New Chemical Exposure Limit section, the Company shall take representative samples of

what the potential exposure of each person who is reasonably likely to be exposed to airborne concentrations of the PMN substances would be if respirators were not worn. The Company shall do so by sampling the breathing zone air of at least one person that represents, and does not underestimate, the potential exposure of every person performing the same or substantially similar operations in each work shift, in each job classification, in each work area (hereinafter identified as an "exposure group") where inhalation exposure to the PMN substances is reasonably likely to occur. The exposure of each person need not be itself directly sampled if that exposure is represented by sampling the exposure of another person in the same exposure group.

(iii) Good Laboratory Practice Standards. Determinations of potential inhalation exposure shall be made according to TSCA Good Laboratory Practice Standards at 40 CFR Part 792 and the sampling and analytical method developed pursuant to subsection (c) of this New Chemical Exposure Limit section. [Certain provisions of the TSCA GLPS applicable to toxicity testing in laboratory animals, such as 40 CFR 792.43 ("Test system care facilities"), 792.45 ("Test system supply facilities") and 792.90 ("Animal and other test system care"), are clearly inapplicable to the NCEL requirements.] However, compliance with TSCA GLPS is not required where exposure monitoring samples are analyzed by a laboratory accredited by either: (A) the American Industrial Hygiene Association ("AIHA") Industrial Hygiene Laboratory Accreditation Program ("IHLAP"); or (B) another comparable program approved in advance in writing by EPA.

(iv) Full Shift Exposure Samples. Representative 8-hour TWA airborne concentrations shall be determined on the basis of samples representing the full shift exposure for

each exposure group.

(2) Initial Monitoring. Before the Company may deviate from the respirator requirements of the Protection in the Workplace section, the Company shall conduct initial exposure monitoring to accurately determine the airborne concentration of the PMN substances for each exposure group in which persons are reasonably likely to be exposed to the PMN substances.

(3) Periodic Monitoring.

(i) If any representative samples taken during the initial exposure monitoring reveal an airborne concentration at or above the action level but at or below the TWA, the Company shall repeat the exposure monitoring for that exposure group at least every 6 months. If the PMN substances are not manufactured, processed, or used at all during a given 6 month calendar period, the Company is not required to conduct exposure monitoring until manufacture, processing, or use of the PMN substances is resumed. However, cessation of manufacturing, processing and use of the PMN substances for less than the 6 month period does not constitute grounds for postponement of the 6 month deadline to conduct exposure monitoring.

(ii) If any representative samples taken during the initial exposure monitoring reveal an airborne concentration above the TWA, the Company shall repeat the exposure monitoring for that exposure group at least every 3 months. If the PMN substances are not manufactured, processed, or used at all during a given 3 month calendar period, the Company is not required to conduct exposure monitoring until manufacture, processing, or use of the PMN substances is resumed. However, cessation of manufacturing, processing and use of the PMN substances for less than the 3 month period does not constitute grounds for postponement of the

3 month deadline to conduct exposure monitoring.

(iii) The Company may alter the exposure monitoring schedule from every 3 months to every 6 months for any exposure group for whom two consecutive measurements taken at least 7 days apart indicate that the potential exposure has decreased to the TWA or below, but is at or above the action level. Where the PMN substances are manufactured, processed, or used in batches of duration less than 7 days, the 2 consecutive measurements may be taken at least 24 hours apart, provided that the measurements accurately reflect the highest peak exposures and variability in exposure.

(4) Termination of Monitoring.

(i) If representative samples taken during the initial exposure monitoring reveal an airborne concentration below the action level, the Company may discontinue monitoring for that exposure group, except when additional exposure monitoring is required by paragraph (d)(5) of this New Chemical Exposure Limit section.

(ii) If representative samples taken during the periodic monitoring reveal that an airborne concentration, as indicated by at least 2 consecutive measurements taken at least 7 days apart, are below the action level, the Company may discontinue the monitoring for that exposure group, except when additional monitoring is required by paragraph (d)(5) of this New Chemical Exposure Limit section. Where the PMN substances are manufactured, processed, or used in batches of duration less than 7 days, the 2 consecutive measurements may be taken at least 24 hours apart, provided that the measurements accurately reflect the highest peak exposures and variability in exposure.

(5) Additional Monitoring.

(i) For a previously monitored exposure group, the Company shall, within 7 days of any of the events listed below in this paragraph (d)(5)(i), conduct the initial exposure monitoring followed by any periodic or additional exposure monitoring required by subsection (d) of this New Chemical Exposure Limit section:

(I) change in the production volume, process, control equipment, personnel or work practices that may reasonably cause new or additional exposures to the PMN substances;

(II) spills, leaks, ruptures or other breakdowns occur that may reasonably cause new or additional exposures to the PMN substances; and

(III) whenever else the Company has any reason to suspect a change that may reasonably result in new or additional exposures to the PMN substances.

(ii) In no event is the additional exposure monitoring requirement in paragraph (d)(5)(i) intended to delay implementation of any necessary cleanup or other remedial action. During any cleanup or remedial operations that may occur before commencing additional exposure monitoring, the Company shall ensure that potentially exposed persons use at least the respiratory protection specified in subsection (e) for the measured airborne concentration, or more protective respiratory equipment deemed appropriate by the best professional judgment of a qualified expert.

(6) Notification of Monitoring Results.

(i) Within 15 working days after receipt of the results of any exposure monitoring required by this Order, the Company shall notify each person whose exposure is represented by that monitoring. The notice shall identify the NCEL, the exposure monitoring results, and any

corresponding respiratory protection required by subsection (e). Affected persons shall be notified in writing either individually or by posting the information in an appropriate and accessible location.

(ii) Whenever the NCEL is exceeded, the written notification required by the preceding paragraph shall describe the action being taken by the Company to reduce inhalation exposure to or below the NCEL, or shall refer to a document available to the person which states the actions to be taken to reduce exposure.

(7) Exemption based on Objective Data. Where the Company has documented and reliable objective data demonstrating that, even under worst-case conditions, employee exposure to the PMN substances will not exceed the action level (defined in paragraph (d)(1)(i)) under the expected handling procedures and conditions for a specific "exposure group" (defined in paragraph (d)(1)(ii)), then that exposure group is exempt from this New Chemical Exposure Limit section (except paragraph (d)(5) "Additional Monitoring" and subsection (f) "NCEL Record-keeping") and the respirator requirements in the Protection in the Workplace section of this Order. Any such objective data must accurately characterize actual employee exposures to the PMN substances and must be obtained under conditions closely resembling the types of materials, processes, control methods, work practices, and environmental conditions in the Company's current workplace operations with the PMN substances. Examples of objective data that may be used to demonstrate that employee exposure will not exceed the action level, even under worst case conditions, include information on the physical and chemical properties of the PMN substances, industry-wide studies, and/or laboratory test results.

(e) Respiratory Protection.

(1) General. Whenever the Company has conducted exposure monitoring at a workplace in accordance with subsection (d) of this New Chemical Exposure Limit section and the measured airborne concentration of the PMN substances for any person who is reasonably likely to be exposed to the PMN substances by inhalation exceeds the NCEL, the Company shall provide those persons the respirators specified in this subsection (e) (rather than the respirator(s) identified in the Protection in the Workplace section of this Order), and shall ensure that the respirators are used (including training, fit testing, and maintenance) in accordance with OSHA and NIOSH respiratory protection requirements at 29 CFR 1910.134 and 42 CFR Part 84. When the Company has not yet measured the airborne concentration of the PMN substances at a workplace in accordance with this New Chemical Exposure Limit section, the Company shall comply with the respirator requirements in the Protection in the Workplace section of this Order at that workplace.

(2) Selection of Appropriate Respiratory Protection. After the Company has conducted exposure monitoring in accordance with subsection (d) of this New Chemical Exposure Limit section, the Company shall select, provide, and ensure that persons who are reasonably likely to be exposed to the PMN substances by inhalation use, at a minimum, the respiratory protection which corresponds in the following table to the measured airborne concentration (or a more protective respirator which corresponds to a concentration higher than measured)

Measured
Concentration
of PMN Substance

Required Respiratory Protection

≤ NCEL

- No respiratory protection is required.

≤ 10 x NCEL

If Data on Cartridge Service Life Testing has been Reviewed and Approved by EPA:

- NIOSH-certified air-purifying, tight-fitting full-face respirator equipped with the appropriate gas/vapor cartridges (organic vapor, acid gas, or substance-specific).

- NIOSH-certified powered air-purifying respirator equipped with a loose fitting hood or helmet and equipped with the appropriate gas/vapor cartridges (organic vapor, acid gas, or substance-specific).

≤ 25 x NCEL

If Data on Cartridge Service Life Testing has been Reviewed and Approved by EPA:

- NIOSH-certified air-purifying, tight-fitting full-face respirator equipped with the appropriate gas/vapor cartridges (organic vapor, acid gas, or substance-specific).

- NIOSH-certified powered air-purifying respirator equipped with a loose-fitting hood or helmet and the appropriate gas/vapor cartridges (organic vapor, acid gas, or substance-specific).

≤ 50 x NCEL

If Data on Cartridge Service Life Testing has been Reviewed and Approved by EPA:

- NIOSH-certified air-purifying, tight-fitting full-face respirator equipped with the appropriate gas/vapor cartridges (organic vapor, acid gas, or substance-specific).

If No Cartridge Service Life Testing is Available:

- NIOSH-certified supplied-air respirator operated in pressure demand or continuous flow mode and equipped with a tight-fitting full facepiece.

≤ 2000 x NCEL

- NIOSH-certified supplied-air respirator operated in pressure demand or

other positive pressure mode and equipped with a tight-fitting full facepiece.

> 2000 x NCEL

- Any self-contained respirator equipped with a full facepiece and operated in a pressure demand or other positive pressure mode.
- Any supplied-air respirator equipped with a full facepiece operated in a pressure demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in a pressure demand or other positive pressure mode.

(3) Reductions in Respiratory Protection. After appropriate respiratory protection has been selected based on the results of actual exposure monitoring conducted at a workplace in accordance with subsection (d) of this New Chemical Exposure Limit section, the Company shall not, at that workplace, use the respiratory protection required by the Protection in the Workplace section of this Order (unless it is the same as required by this New Chemical Exposure Limit section). Before the Company may make any reduction in any respiratory protection selected pursuant to this New Chemical Exposure Limit section, the Company must verify, by 2 consecutive measurements taken at least 7 days apart, that the new respiratory protection is appropriate in accordance with paragraph (c)(2). Where the PMN substances is manufactured, processed, or used in batches of duration less than 7 days, the 2 consecutive measurements may be taken at least 24 hours apart, provided that the measurements accurately reflect the highest peak exposures and variability in exposure.

(4) Special Situations.

(i) Measurements Outside Quantitation Limits. When a value less than the lower quantitation limit ("LQL") of the analytical method (as described in paragraph (c)(4)(ii)) is

measured, the Company shall estimate potential exposure using generally established and accepted statistical methods. If the Company obtains an exposure monitoring sample that is more than 10% above the actual upper quantitation limit ("UQL") of the analytical method, the Company must ensure that its workers wear at least a NIOSH-certified supplied-air respirator operated in pressure demand or other positive pressure mode and equipped with a tight-fitting full facepiece. Any reductions in this respiratory protection must comply with paragraph (e)(3). The Company may submit an improved analytical method provided that it complies fully with subsection (c) of this New Chemical Exposure Limit section, including the verification required by subsection (c)(3).

(ii) Cleanup and Remedial Actions. During any special cleanup or other remedial actions that may occur before commencing additional exposure monitoring (as discussed in paragraph (d)(5)(ii)), the Company shall ensure that potentially exposed persons use at least the respiratory protection specified above in this subsection (e) for the measured airborne concentration, or more protective respiratory equipment deemed appropriate by the best professional judgment of a qualified expert.

(f) NCEL Recordkeeping.

(1) Whenever the Company elects to comply with this New Chemical Exposure Limit section rather than the respirator requirements in the Protection in the Workplace section of this Order, the Company shall maintain the following records until 30 years after the date they are created, and shall make them available for inspection and copying by EPA in accordance with section 11 of TSCA:

(i) A copy of the sampling and analytical methods used and continuing evidence

of their accuracy over time as required by section (c);

(ii) Records documenting compliance with the analytical method verification requirements of subsection (c)(3), including copies of the signed certification statement and the verification results obtained by both laboratories;

(iii) Records documenting either compliance with the Good Laboratory Practice Standards at 40 CFR Part 792, or use of a laboratory accredited by the American Industrial Hygiene Association ("AIHA") or another comparable program approved in advance in writing by EPA. Where the Company elects to not comply with TSCA GLPS, such records shall include the written accreditation from the AIHA or the written approval from EPA.

(iv) Records documenting all exposure monitoring dates, duration, and results of each sample taken;

(v) Records documenting the name, address, work shift, job classification, and work area of the person monitored and of all other persons whose exposures the monitoring is intended to represent;

(vi) Any conditions that might have affected the monitoring results;

(vii) Notification of exposure monitoring results required by paragraph (d)(6);

(viii) Records documenting any changes in the production, process, control equipment, personnel or work practices that may reasonably cause new or additional exposures to the PMN substances;

(ix) Records documenting any spills, leaks, ruptures or other breakdowns that may cause new or additional exposure;

(x) The type of respiratory protective devices worn by the monitored person, if any;

(xi) Records documenting any actions taken to mitigate exposures to the PMN substances;

(xii) Records documenting reliance on the objective data exemption in paragraph (d)(7), including: (A) the source of the data, (B) protocols and results of any relevant testing or analysis, (C) a description of the operation exempted and how the data demonstrate that employee exposures will not exceed the action level, (D) other data relevant to the operations, materials and employee exposures covered by the exemption.

MANUFACTURING

(a) (1) Prohibition. The Company shall not cause, encourage, or suggest the manufacture or import of the PMN substances by any other person.

(2) Sunset Following SNUR. Subparagraph (a)(1) shall expire 75 days after promulgation of a final significant new use rule ("SNUR") governing the PMN substances under section 5(a)(2) of TSCA unless the Company is notified on or before that day of an action in a Federal Court seeking judicial review of the SNUR. If the Company is so notified, subparagraph (a)(1) shall not expire until EPA notifies the Company in writing that all Federal Court actions involving the SNUR have been resolved and the validity of the SNUR affirmed.

(3) Notice of SNUR. When EPA promulgates a final SNUR for the PMN substances and subparagraph (a)(1) expires in accordance with subparagraph (a)(2), the Company shall notify each person whom it causes, encourages or suggests to manufacture or import the PMN substances of the existence of the SNUR.

CONTROL OF EFFLUENT & EMISSIONS

(a) The Company shall recover and capture (destroy) or recycle the PMN substances at an overall efficiency of 99% from all the effluent process streams and the air emissions (point source and fugitive).

DISTRIBUTION

(a) Distribution Requirements. Except as provided in paragraph (b), the Company shall distribute the PMN substances outside the Company, only to a person who has agreed in writing prior to the date of distribution, to:

(1) Comply with the same requirements and restrictions, if any, required of the Company in the Protection in the Workplace and the New Chemical Exposure Limit sections of this Order;

(2) Distribute the PMN substances only to a person who will either recover and capture (destroy) or recycle the PMN substances from all effluent process streams and air emissions (point source and fugitive) at an overall efficiency of 99%; and

(3) Distribute the PMN substance P-08-509 in an aqueous dispersion of the polymer product or on a heat treated solid product such that the contents polymer residual P-08-508/509 cumulative total [] are below 200 ppb level using the ASE method developed by Larsen et al¹ with the level of quantification (LOQ) for the standard solution at 0.5 ppb. If non-heat treated solid polymer is distributed by the Company, such person shall not further distribute until heat treatment is performed at temperature and residence time sufficient to produce a product with P08-508/509 cumulative residual levels equivalent to the heat treated

¹Larsen et al, "Efficient "total" extraction of perfluorooctanoate from polytetrafluoroethylene fluoropolymer", *Analyst*, 2006, 131, 1105-1108.

polymer distributed by the Company, (i.e., below 200 ppb).

(b) Temporary Transport and Storage. Notwithstanding paragraph (a), the Company may distribute the PMN substances outside the Company for temporary transport and storage in sealed containers provided the following two conditions are met:

(1) Subsequent to any such exempt temporary transport or storage of sealed containers, the PMN substances may be distributed only to the Company or a person who has given the Company the written agreement required by paragraph (a).

(2) Any human exposure or environmental release resulting from opening the sealed containers and removing or washing out the PMN substances may occur only while the PMN substances is in the possession and control of the Company or a person who has given the Company the written agreement required by paragraph (a).

(c) Recipient Non-Compliance. If, at any time after commencing distribution in commerce of the PMN substances, the Company obtains knowledge that a recipient of the substance has failed to comply with any of the conditions specified in paragraph (a) of this Distribution section or, after paragraph (a)(1) expires in accordance with subparagraph (d)(1), has engaged in a significant new use of the PMN substances (as defined in 40 CFR Part 721, Subpart E) without submitting a significant new use notice to EPA, the Company shall cease supplying the substance to that recipient, unless the Company is able to document each of the following:

(1) That the Company has, within 5 working days, notified the recipient in writing that the recipient has failed to comply with any of the conditions specified in paragraph (a) of this Distribution section, or has engaged in a significant new use of the PMN substances without

submitting a significant new use notice to EPA.

(2) That, within 15 working days of notifying the recipient of the noncompliance, the Company received from the recipient, in writing, a statement of assurance that the recipient is aware of the terms of paragraph (a) of this Distribution section and will comply with those terms, or is aware of the terms of the significant new use rule for the PMN substances and will not engage in a significant new use without submitting a significant new use notice to EPA.

(3) If, after receiving a statement of assurance from a recipient under subparagraph (c)(2) of this Distribution section, the Company obtains knowledge that the recipient has failed to comply with any of the conditions specified in paragraph (a) of this Distribution section, or has engaged in a significant new use of the PMN substances without submitting a significant new use notice to EPA, the Company shall cease supplying the PMN substances to that recipient, shall notify EPA of the failure to comply, and shall resume supplying the PMN substances to that recipient only upon written notification from the Agency.

(d) Sunset Following SNUR. (1) Paragraph (a)(1) of this Distribution section shall expire 75 days after promulgation of a final SNUR for the PMN substances under section 5(a)(2) of TSCA, unless the Company is notified on or before that day of an action in a Federal Court seeking judicial review of the SNUR. If the Company is so notified, paragraph (a)(1) of this Distribution section shall not expire until EPA notifies the Company in writing that all Federal Court actions involving the SNUR have been resolved and the validity of the SNUR affirmed.

(2) When EPA promulgates a final SNUR for the PMN substances and paragraph (a)(1) of this Distribution section expires in accordance with subparagraph (d)(1), the Company shall notify each person to whom it distributes the PMN substances of the existence of the SNUR. Such

notification must be in writing and must specifically include all limitations contained in the SNUR which are defined as significant new uses, and which would invoke significant new use notification to EPA for the PMN substances. Such notice must also reference the publication of the SNUR for this PMN substances in either the Federal Register or the Code of Federal Regulations. After promulgation of a SNUR and expiration of subparagraph (a)(1), such notice may substitute for the written agreement required in the introductory clause of paragraph (a); so that, if the Company provides such notice to the persons to whom it distributes the PMN substances, then the Company is not required to obtain from such persons the written agreement specified in paragraph (a).

III. RECORDKEEPING

(a) Records. The Company shall maintain the following records until 5 years after the date they are created and shall make them available for inspection and copying by EPA in accordance with section 11 of TSCA:

(1) Exemptions. Records documenting that the PMN substances did in fact qualify for any one or more of the exemptions described in Section I, Paragraph (b) of this Order. Such records must satisfy all the statutory and regulatory recordkeeping requirements applicable to the exemption being claimed by the Company. Any amounts or batches of the PMN substances eligible for the Export exemption in Section I, Paragraph (b)(3) of this Order, are exempt from all the requirements in this Recordkeeping section, if the Company maintains, for 5 years from the date of their creation, copies of the export label and export notice to EPA, required by TSCA sections 12(a)(1)(B) and 12(b), respectively. Any amounts or batches of the PMN substances eligible for the Research and Development exemption in Section I, Paragraph (b)(2) of this Order, are exempt from all the requirements in this Recordkeeping section, if the Company maintains, for

5 years from the date of their creation, the records required by 40 CFR 720.78(b). For any amounts or batches of the PMN substances claimed to be eligible for any other exemption described in Section I, Paragraph (b) of this Order, the Company shall keep records demonstrating qualification for that exemption as well as the records specified in paragraphs (2) and (3) below, but is exempt from the other recordkeeping requirements in this Recordkeeping section;

(2) Records documenting the manufacture and importation volume of the PMN substances and the corresponding dates of manufacture and import;

(3) Records documenting the names and addresses (including shipment destination address, if different) of all persons outside the site of manufacture or import to whom the Company directly sells or transfers the PMN substances, the date of each sale or transfer, and the quantity of the substance sold or transferred on such date;

(4) Records documenting the address of all sites of manufacture, import, processing, and use;

(5) Records documenting establishment and implementation of a program for the use of any applicable personal protective equipment required pursuant to the Protection in the Workplace section of this Order;

(6) Records documenting the determinations required by the Protection in the Workplace section of this Order that chemical protective clothing is impervious to the PMN substances;

(7) Records required by paragraph (f). of the New Chemical Exposure Limits section of this Order, if applicable;

(8) Records documenting compliance with any applicable manufacturing, processing, use, and distribution restrictions in the Manufacturing and Distribution sections of this Order, including distributees' written agreement to comply with the Distribution section of this Order;

(9) Records documenting compliance with the Control of Effluent & Emissions section of this Order;

(10) Copies of any Transfer Documents and notices required by the Successor Liability section of this Order, if applicable; and

(11) The Company shall keep a copy of this Order at each of its sites where the PMN substances are manufactured or imported.

(b) Applicability. The provisions of this Recordkeeping Section are applicable only to activities of the Company and its Contract Manufacturer, if applicable, and not to activities of the Company's customers.

(c) OMB Control Number. Under the Paperwork Reduction Act and its regulations at 5 CFR Part 1320, particularly 5 CFR 1320.5(b), the Company is not required to respond to this "collection of information" unless this Order displays a currently valid control number from the Office of Management and Budget (OMB), and EPA so informs the Company. The "collection of information" required in this TSCA §5(e) Consent Orders has been approved under currently valid OMB Control Number 2070-0012.

IV. REQUESTS FOR PRE-INSPECTION INFORMATION

(a) EPA's Request for Information. Pursuant to section 11 of TSCA and 40 CFR 720.122, EPA may occasionally conduct on-site compliance inspections of Company facilities and conveyances associated with the PMN substances. To facilitate such inspections, EPA personnel may contact the Company in advance to request information pertinent to the scheduling and conduct of such

inspections. Such requests may be written or oral. The types of information that EPA may request may include, but are not limited to, the following:

(i) Expected dates and times when the PMN substances will be in production within the subsequent 12 months;

(ii) Current workshift schedules for workers who are involved in activities associated with the PMN substances and may reasonably be exposed to the PMN substances;

(iii) Current job titles or categories for workers who are involved in activities associated with the PMN substances and may reasonably be exposed to the PMN substances;

(iv) Existing exposure monitoring data for workers who are involved in activities associated with the PMN substances and may reasonably be exposed to the PMN substances;

(v) Records required by the Recordkeeping section of this Order; and/or

(vi) Any other information reasonably related to determining compliance with this Order or conducting an inspection for that purpose.

(b) Company's Response. The Company shall respond to such requests within a reasonable period of time, but in no event later than 30 days after receiving EPA's request. When requested in writing by EPA, the Company's response shall be in writing. To the extent the information is known to or reasonably ascertainable to the Company at the time of the request, the Company's response shall demonstrate a good faith effort to provide reasonably accurate and detailed answers to all of EPA's requests.

(c) Confidential Business Information. Any Confidential Business Information ("CBI") that the Company submits to EPA pursuant to paragraph (b) shall be protected in accordance with §14 of

V. SUCCESSOR LIABILITY UPON TRANSFER OF CONSENT ORDER

(a) **Scope.** This section sets forth the procedures by which the Company's rights and obligations under this Order may be transferred when the Company transfers its interests in the PMN substances, including the right to manufacture the PMN substances, to another person outside the Company (the "Successor in Interest").

(b) **Relation of Transfer Date to Notice of Commencement ("NOC").**

(1) **Before NOC.** If the transfer from the Company to the Successor in Interest is effective before EPA receives a notice of commencement of manufacture or import ("NOC") for the PMN substances from the Company pursuant to 40 CFR 720.102, the Successor in Interest must submit a new PMN to EPA and comply fully with Section 5(a)(1) of TSCA and 40 CFR part 720 before commencing manufacture or import of the PMN substances.

(2) **After NOC.** If the transfer from the Company to the Successor in Interest is effective after EPA receives a NOC, the Successor in Interest shall comply with the terms of this Order and shall not be required to submit a new PMN to EPA.

(c) **Definitions.** The following definitions apply to this Successor Liability section of the Order:

(1) **"Successor in Interest"** means a person outside the Company who has acquired the Company's full interest in the rights to manufacture the PMN substances, including all ownership rights and legal liabilities, through a transfer document signed by the Company, as transferor, and the Successor in Interest, as transferee. The term excludes persons who acquire less than the full

interest of the Company in the PMN substances, such as a licensee who has acquired a limited license to the patent or manufacturing rights associated with the PMN substances. A Successor in Interest must be incorporated, licensed, or doing business in the United States in accordance with 40 CFR 720.22(a)(3).

(2) "Transfer Document" means the legal instrument(s) used to convey the interests in the PMN substances, including the right to manufacture the PMN substances, from the Company to the Successor in Interest.

(d) Notices.

(1) Notice to Successor in Interest. On or before the effective date of the transfer, the Company shall provide to the Successor in Interest, by registered mail, a copy of the Consent Order and the "Notice of Transfer" document which is incorporated by reference as Attachment C to this Order.

(2) Notice to EPA. Within 10 business days of the effective date of the transfer, the Company shall, by registered mail, submit the fully executed Notice of Transfer document to: U.S. Environmental Protection Agency, New Chemicals Branch (7405), 1200 Pennsylvania Avenue, N.W., Washington, D.C. 20460.

(3) Transfer Document. Copies of the Transfer Document must be maintained by the Successor in Interest at its principal place of business, and at all sites where the PMN substances is manufactured or imported. Copies of the Transfer Document must also be made available for inspection pursuant to Section 11 of TSCA, must state the effective date of transfer, and must contain provisions which expressly transfer liability for the PMN substances under the terms of this Order from the Company to the Successor in Interest.

(e) Liability.

(1) The Company shall be liable for compliance with the requirements of this Order until the effective date of the transfer described above.

(2) The Successor in Interest shall be liable for compliance with the requirements of this Order effective as of the date of transfer.

(3) Nothing in this section shall be construed to prohibit the Agency from taking enforcement action against the Company after the effective date of the transfer for actions taken, or omissions made, during the time in which the Company manufactured, processed, used, distributed in commerce, or disposed of the PMN substances pursuant to the terms of this Consent Order.

(f) Obligations to Submit Test Data under Consent Order. If paragraph (d) of the Testing section of this Consent Order requires the Company to submit test data to EPA at a specified production volume ("test trigger"), the aggregate volume of the PMN substances manufactured and imported by the Company up to the date of transfer shall count towards the test trigger applicable to the Successor in Interest.

VI. MODIFICATION AND REVOCATION OF CONSENT ORDER

The Company may petition EPA at any time, based upon new information on the health effects of, or human exposure to, the PMN substances, to modify or revoke substantive provisions of this Order. The exposures and risks identified by EPA during its review of the PMN substances and the information EPA determined to be necessary to evaluate those exposures and risks are described in the preamble to this Order. However, in determining whether to amend or revoke this Order, EPA will consider all relevant information available at the time the Agency makes that

determination, including, where appropriate, any reassessment of the test data or other information that supports the findings in this Order, an examination of new test data or other information or analysis, and any other relevant information.

EPA will issue a modification or revocation if EPA determines that the activities proposed therein will not present an unreasonable risk of injury to health or the environment and will not result in significant or substantial human exposure or substantial environmental release in the absence of data sufficient to permit a reasoned evaluation of the health or environmental effects of the PMN substances.

In addition, the Company may petition EPA at any time to make other modifications to the language of this Order. EPA will issue such a modification if EPA determines that the modification is useful, appropriate, and consistent with the structure and intent of this Order as issued.

VII. EFFECT OF CONSENT ORDER

By consenting to the entry of this Order, the Company waives its rights to file objections to this Order pursuant to section 5(e)(1)(C) of TSCA, to receive service of this Order no later than 45 days before the end of the review period pursuant to section 5(e)(1)(B) of TSCA, and to challenge the validity of this Order in any subsequent action. Consenting to the entry of this Order, and agreeing to be bound by its terms, do not constitute an admission by the Company as to, the facts or conclusions underlying the Agency's determinations in this proceeding. This waiver does not affect any other rights that the Company may have under TSCA.

1/26/09

Date

/s/

Jim Willis, Director
Chemical Control Division
Office of Pollution Prevention and Toxics

1/28/09

Date

/s/

Name: James R. Hoover

Title: Global Regulatory Manager

Company: DuPont Company

ATTACHMENT A

DEFINITIONS

[Note: The attached Order may not contain some of the terms defined below.]

"Chemical name" means the scientific designation of a chemical substance in accordance with the nomenclature system developed by the International Union of Pure and Applied Chemistry or the Chemical Abstracts Service's rules of nomenclature, or a name which will clearly identify a chemical substance for the purpose of conducting a hazard evaluation.

"Chemical protective clothing" means items of clothing that provide a protective barrier to prevent dermal contact with chemical substances of concern. Examples can include, but are not limited to: full body protective clothing, boots, coveralls, gloves, jackets, and pants.

"Company" means the person or persons subject to this Order.

"Commercial use" means the use of a chemical substance or any mixture containing the chemical substance in a commercial enterprise providing saleable goods or a service to consumers (e.g., a commercial dry cleaning establishment or painting contractor).

"Common name" means any designation or identification such as code name, code number, trade name, brand name, or generic chemical name used to identify a chemical substance other than by its chemical name.

"Consumer" means a private individual who uses a chemical substance or any product containing the chemical substance in or around a permanent or temporary household or residence, during recreation, or for any personal use or enjoyment.

"Consumer product" means a chemical substance that is directly, or as part of a mixture, sold or made available to consumers for their use in or around a permanent or temporary household or residence, in or around a school, or in recreation.

"Container" means any bag, barrel, bottle, box, can, cylinder, drum, reaction vessel, storage tank, or the like that contains a hazardous chemical. For purposes of this section, pipes or piping systems, and engines, fuel tanks, or other operating systems in a vehicle, are not considered to be containers.

"Contract Manufacturer" means a person, outside the Company, who is authorized to manufacture and import the PMN substance under the conditions specified in Part II. of this Consent Order and in the Consent Order for Contract Manufacturer.

"Identity" means any chemical or common name used to identify a chemical substance or a mixture containing that substance.

"Immediate use." A chemical substance is for the "immediate use" of a person if it is under the control of, and used only by, the person who transferred it from a labeled container and will only be used by that person within the work shift in which it is transferred from the labelled container.

"Impervious." Chemical protective clothing is "impervious" to a chemical substance if the substance causes no chemical or mechanical degradation, permeation, or penetration of the chemical protective clothing under the conditions of, and the duration of, exposure.

"Manufacturing stream" means all reasonably anticipated transfer, flow, or disposal of a chemical substance, regardless of physical state or concentration, through all intended operations of manufacture, including the cleaning of equipment.

"MSDS" means material safety data sheet, the written listing of data for the chemical substance.

"NIOSH" means the National Institute for Occupational Safety and Health of the U.S. Department of Health and Human Services.

"Non-enclosed process" means any equipment system (such as an open-top reactor, storage tank, or mixing vessel) in which a chemical substance is manufactured, processed, or otherwise used where significant direct contact of the bulk chemical substance and the workplace air may occur.

"Non-industrial use" means use other than at a facility where chemical substances or mixtures are manufactured, imported, or processed.

"PMN substance" means the chemical substance described in the Premanufacture notice submitted by the Company relevant to this Order.

"Personal protective equipment" means any chemical protective clothing or device placed on the body to prevent contact with, and exposure to, an identified chemical substance or substances in the work area. Examples include, but are not limited to, chemical protective clothing, aprons, hoods, chemical goggles, face splash shields, or equivalent eye protection, and various types of respirators. Barrier creams are not included in this definition.

"Process stream" means all reasonably anticipated transfer, flow, or disposal of a chemical substance, regardless of physical state or concentration, through all intended operations of processing, including the cleaning of equipment.

"Scientifically invalid" means any significant departure from the EPA-approved protocol or the Good Laboratory Practice Standards at 40 CFR Part 792 without prior or subsequent Agency approval that prevents a reasoned evaluation of the health or environmental effects of the PMN substance.

"Scientifically equivocal data" means data which, although developed in apparent conformity with the Good Laboratory Practice Standards and EPA-approved protocols, are inconclusive, internally inconsistent, or otherwise insufficient to permit a reasoned evaluation of the potential risk of injury to human health or the environment of the PMN substance.

"Sealed container" means a closed container that is physically and chemically suitable for long-term containment of the PMN substance, and from which there will be no human exposure to, nor environmental release of, the PMN substance during transport and storage.

"Use stream" means all reasonably anticipated transfer, flow, or disposal of a chemical substance, regardless of physical state or concentration, through all intended operations of industrial, commercial, or consumer use.

"Waters of the United States" has the meaning set forth in 40 CFR 122.2.

"Work area" means a room or defined space in a workplace where the PMN substance is manufactured, processed, or used and where employees are present.

"Workplace" means an establishment at one geographic location containing one or more work areas.

ATTACHMENT B

STATISTICAL ANALYSIS OF NCEL's ANALYTICAL METHOD VERIFICATION RESULTS

This Attachment describes the statistical technique (with examples) for comparing the analytical results obtained by two laboratories pursuant to paragraph (c)(3)(vii) of the New Chemical Exposure Limit section of this Order.

STATISTICAL TECHNIQUE

To obtain two-sample t test with unequal variances, perform the following operations:

- Compute means of the data measured by two laboratories.
- Compute mean squares

$$S_i^2 = \sum (\bar{X}_i - X_i)^2 / (n_i - 1), i=1, 2$$

- Form the ratio

$$T = (\bar{X}_1 - \bar{X}_2) / (W_1 + W_2)^{1/2}$$

- Compute degrees of freedom

$$f = (W_1 + W_2)^2 / [W_1^2 / (n_1 - 1) + W_2^2 / (n_2 - 1)]$$

where,

$$W_i = S_i^2 / n_i, i = 1, 2$$

\bar{X}_1 = Average of the results from the company laboratory

\bar{X}_2 = Average of the results from the independent laboratory

n_1 = Number of samples analyzed by the company laboratory

n_2 = Number of samples analyzed by the independent laboratory.

Then compare the absolute value of T to the 97.5 percentile point of a t distribution with f degrees of freedom. If the absolute value exceeds the 97.5 percentile point, the results measured

by two laboratories are significantly different at 95% level. Otherwise, they are not significantly different. In general, f may not be an integer. Use interpolation to obtain the 97.5 percentile point of a t distribution with f degrees of freedom.

EXAMPLES -- The following examples (based on simulated data) illustrate the method:

Example 1

<u>Data Set 1</u>		<u>Data Set 2</u>	
	80.56		97.11
	100.01		102.13
	86.04		99.83
	52.61		97.83
	84.85		105.44
	95.75		100.04
$\bar{X}_1 = 83.30$	$n_1 = 6$	$\bar{X}_2 = 100.40$	$n_2 = 6$
$S_1^2 = 278.72$	$W_1 = 46.25$	$S_2^2 = 9.26$	$W_2 = 1.54$
Absolute value of $T = 2.467$		$f = 5.33$	

The t table shows that the 97.5 percentile point is 2.571 and 2.447 for 5 and 6 degrees of freedom, respectively. For 5.33 degrees of freedom, the 97.5 percentile point will be approximately 2.530 which is greater than the absolute value of T , 2.467. Hence, the means of two data sets are not significantly different at the 5% level.

However, if this problem had been treated as an ordinary two-sample t test, the means would be significantly different at the 5% level because the absolute of T is greater than 2.228, the 97.5 percentile point for the t distribution with 10 degrees of freedom.

Example 2

<u>Data Set 1</u>	<u>Data Set 2</u>
82.87	108.05
101.85	96.51
87.44	100.04
99.68	104.33
101.15	110.32
99.21	107.00

$$\bar{X}_1 = 95.37 \quad n_1 = 6 \quad \bar{X}_2 = 104.37 \quad n_2 = 6$$

$$S_1^2 = 65.59 \quad W_1 = 10.93$$

$$S_2^2 = 27.25$$

$$W_2 = 4.54$$

$$\text{Absolute value of } T = 2.290$$

$$f = 8.54$$

The t table shows that for 8 and 9 degrees of freedom the 97.5 percentile point is 2.306 and 2.262, respectively. For 8.54 degrees of freedom the 97.5 percentile point will be approximately 2.282 which is less than the absolute value of T, 2.290. Hence, the means of two data sets are significantly different at the 5% level.

ATTACHMENT C

NOTICE OF TRANSFER
OF
TOXIC SUBSTANCES CONTROL ACT
SECTION 5(e) CONSENT ORDER

Company (Transferor)

PMN Number

1. Transfer of Manufacture Rights. Effective on _____, the Company did sell or otherwise transfer to _____, ("Successor in Interest") the rights and liabilities associated with manufacture of the above-referenced chemical substance, which was the subject of a premanufacture notice ("PMN") and is governed by a Consent Order issued by the U.S. Environmental Protection Agency ("EPA") under the authority of §5(e) of the Toxic Substances Control Act (TSCA, 15 U.S.C. §2604(e)).

2. Assumption of Liability. The Successor in Interest hereby certifies that, as of the effective date of transfer, all actions or omissions governed by the applicable Consent Order limiting manufacture, processing, use, distribution in commerce and disposal of the PMN substance, shall be the responsibility of the Successor in Interest. Successor in Interest also certifies that it is incorporated, licensed, or doing business in the United States in accordance with 40 CFR 720.22(a)(3).

3. Confidential Business Information. The Successor in Interest hereby:

___ reasserts,

___ relinquishes, or

___ modifies

all Confidential Business Information ("CBI") claims made by the Company, pursuant to Section 14 of TSCA and 40 CFR part 2, for the PMN substance(s). Where "reasserts" or "relinquishes" is indicated, that designation shall be deemed to apply to all such claims. Where "modifies" is indicated, such modification shall be explained in detail in an attachment to this Notice of Transfer. Information which has been previously disclosed to the public (e.g., a chemical identity that was not claimed as CBI by the original submitter) would not subsequently be eligible for confidential treatment under this Notice of Transfer.

**TOXIC SUBSTANCES CONTROL ACT
SECTION 5(e) CONSENT ORDER**

**NOTICE OF TRANSFER
(continued)**

Company (Transferor)

PMN Number

Signature of Authorized Official

Date

Printed Name of Authorized Official

Title of Authorized Official

Successor in Interest

Signature of Authorized Official

Date

Printed Name of Authorized Official

Title of Authorized Official

Address

City, State, Zip Code

**TOXIC SUBSTANCES CONTROL ACT
SECTION 5(e) CONSENT ORDER**

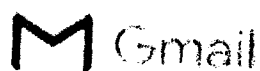
**NOTICE OF TRANSFER
(continued)**

Successor's Technical Contact

Address

City, State, Zip Code

Phone



Linda Miles <milesfirm@gmail.com>

Fwd: Dupont PMN

4 messages

George House <GHOUSE@brookspierce.com>

Wed, Jun 14, 2017 at 9:52 AM

To: Linda Miles <milesfirm@gmail.com>, Beth Eckert <Beth.Eckert@cfpua.org>

See my email confirmation my librarian of no change to EPA CO and summary. Note two chemical formulas - I had not seen these before. Hepta denotes 7 and tetra denotes 4.

George House

t: 336.271.3114

f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

Begin forwarded message:

From: Jayant Joshi <JJOSHI@brookspierce.com>
Date: June 14, 2017 at 9:32:30 AM EDT
To: George House <GHOUSE@brookspierce.com>
Cc: "V. Randall Tinsley" <RTINSLEY@brookspierce.com>
Subject: RE: Dupont PMN

No, I did not see any modifications to the original order in any of the documents I pulled.

Also - The attached dockets only reference the 1/28/09 order, and answer "No" in the section that asks if the original order has been modified or revoked.

Jayant Joshi, Librarian & Research Specialist

Confidentiality Notice:

The information contained in this e-mail transmittal is privileged and confidential intended for the addressee only. If you are neither the intended recipient nor the employee or agent responsible for delivering this e-mail to the intended recipient, any disclosure of this information in any way or taking of any action in reliance on this information is strictly prohibited. If you have received this e-mail in error, please notify the person transmitting the information immediately.

This e-mail message has been scanned and cleared by MailMarshal SMTP.

8 attachments



Beth Eckert <Beth.Eckert@cfpua.org>
 To: George House <GHOUSE@brookspierce.com>
 Cc: Linda Miles <milesfirm@gmail.com>

Wed, Jun 14, 2017 at 10:01 AM

Thanks George

Beth Eckert
 [Quoted text hidden]

<image001.jpg>

t: 336.232.4646
 f: 336.232.9146

2000 Renaissance Plaza
 230 North Elm Street
 Greensboro, NC 27401

P.O. Box 26000 (27420)

From: George House
Sent: Wednesday, June 14, 2017 5:06 AM
To: Jayant Joshi <JJOSHI@brookspierce.com>
Cc: V. Randall Tinsley <RTINSLEY@brookspierce.com>
Subject: Dupont PMN

In the subsequent docs you found, is there any amendment to the original Consent Decree?

George House

<image004.jpg>

t: 336.271.3114
f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

<p-08-508 Docket.pdf>

<p-08-509 Docket.pdf>

milesfirm@gmail.com <milesfirm@gmail.com>
To: adamsjh@corning.com

Wed, Jun 14, 2017 at 11:34 AM

Sent from my iPhone

Begin forwarded message:

From: Beth Eckert <Beth.Eckert@cfpua.org>
Date: June 14, 2017 at 10:01:20 AM EDT
To: George House <GHOUSE@brookspierce.com>
Cc: Linda Miles <milesfirm@gmail.com>
Subject: Re: Dupont PMN

[Quoted text hidden]

Linda Miles <milesfirm@gmail.com>
To: Donna Pope <Donna.pope@cfpua.org>

Wed, Jun 14, 2017 at 12:48 PM

[Quoted text hidden]

8 attachments

BROOKS  PIERCE  4K

BROOKS  PIERCE  4K

 ATT00001.htm
2K

 ATT00002.htm
1K

 p-08-508 Docket.pdf
7K

 ATT00003.htm
1K

 p-08-509 Docket.pdf
6K

 ATT00004.htm
1K

Consent Orders

- **Chemical Name:** Azanium, 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate
- **Chemical Identifier:** 62037-80-3
- **Chemical Category:** Perfluoro Compounds; PBT chemicals;

[View Consent Orders](#)

What type of TSCA Section 5(e) Consent Order was developed for this chemical substance?:

Risk-based and Exposure-based Consent Order

Consent Order for: Azanium, 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate , 62037-80-3

Effective Date of TSCA Section 5(e) Consent Order: 1/28/2009

PMN Number: P-08-0509

Has the chemical been commenced?: Yes

Functional Use: Polymerization aid (generic)

What are the health or environmental toxicity concerns?:

- Aquatic and/or terrestrial toxicity:
- Cancer effects:
- Developmental/reproduction:
- Internal organs (e.g., liver, blood, kidney, etc.)/systemic toxicity:
- Lung toxicity (including lung overload):
- Mutagenicity:
- Persistent, Bioaccumulative, Toxic (PBT) properties:

What is the health or environmental concern based on?:

- Analog data:
- PBT chemicals:
- Perfluoro Compounds:
- Chemical testing:
- Physical/chemical properties:

Limitations on manufacture (including import), processing, distribution in commerce, use, or disposal pending submission and evaluation of information:

- As an alternative to using respirators, maintain workplace airborne concentrations of the PMN substance at or below a New Chemical Exposure Limit (NCEL): of 0.01 milligrams per cubic meter as an 8-hour time weighted average (TWA) verified by actual exposure monitoring:
- Disposal from manufacturing, processing, and/or use that differ from: the recovery and capture (destruction) or recycle of the PMN substance at an overall efficiency of 99% from all effluent streams and air emissions (point source and fugitive):
- Production volume greater than: the confidential aggregate manufacture volume identified in the consent order:
- Recordkeeping for all manufacturers and processors:

Has EPA modified or revoked the Consent Order based on submission of the listed testing?:

- No:

Consent Orders

- **Chemical Name:** 2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
- **Chemical Identifier:** 13252-13-6
- **Chemical Category:** Perfluoro Compounds; PBT chemicals;

[View Consent Orders](#)

What type of TSCA Section 5(e) Consent Order was developed for this chemical substance?:

Risk-based and Exposure-based Consent Order

Consent Order for: 2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid , 13252-13-6

Effective Date of TSCA Section 5(e) Consent Order: 1/28/2009

PMN Number: P-08-0508

Has the chemical been commenced?: Yes

Functional Use: Intermediate for polymerization aid (generic)

What are the health or environmental toxicity concerns?:

- Aquatic and/or terrestrial toxicity:
- Cancer effects:
- Developmental/reproduction:
- Internal organs (e.g., liver, blood, kidney, etc.)/systemic toxicity:
- Lung toxicity (including lung overload):
- Mutagenicity:
- Persistent, Bioaccumulative, Toxic (PBT) properties:

What is the health or environmental concern based on?:

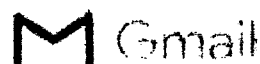
- Analog data:
- PBT chemicals:
- Perfluoro Compounds:
- Chemical testing:
- Physical/chemical properties:

Limitations on manufacture (including import), processing, distribution in commerce, use, or disposal pending submission and evaluation of information:

- As an alternative to using respirators, maintain workplace airborne concentrations of the PMN substance at or below a New Chemical Exposure Limit (NCEL): of 0.01 milligrams per cubic meter as an 8-hour time weighted average (TWA) verified by actual exposure monitoring:
- Disposal from manufacturing, processing, and/or use that differ from: the recovery and capture (destruction) or recycle of the PMN substance at an overall efficiency of 99% from all effluent streams and air emissions (point source and fugitive):
- Production volume greater than: the confidential aggregate manufacture volume identified in the consent order:
- Recordkeeping for all manufacturers and processors:

Has EPA modified or revoked the Consent Order based on submission of the listed testing?:

- No:



Linda Miles <milesfirm@gmail.com>

Chemours NPDES Permit1 message

George House <GHOUSE@brookspierce.com>

Mon, Jun 12, 2017 at 5:36 PM

To: "milesfirm@gmail.com" <milesfirm@gmail.com>

Cc: "Beth Eckert (Beth.Eckert@cfpua.org)" <Beth.Eckert@cfpua.org>, "V. Randall Tinsley" <RTINSLEY@brookspierce.com>

I have read through this twice and Randy has read it as well.

Notes:

- 1) no reference to the 99% efficiency required by EPA.
- 2) no sampling for he GenX
- 3) only sampling on a monthly grab basis for PFOA (See A. (3)) which is the long chain chemical they stopped using in or around 2006-10. Hopefully, there is 0 PFOA.
- 4) the outfall is the WS-IV if from outfall 002 which is the manufacturing plant combined with the storm water/cooling water flow. There is very little sampling of the manufacturing plant discharge into 001. (See A.(1))

From what is required by this Permit there is no conceivable way you could determine 99% efficiency removal of GenX.

We need to see their permit application and those are hard to come by (we are trying) and see what if anything Dupont said about GenX.

George House

Brooks Pierce

t: 336.271.3114

f: 336.232.9114


2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

Confidentiality Notice:

The information contained in this e-mail transmittal is privileged and confidential intended for the addressee only. If you are neither the intended recipient nor the employee or agent responsible for delivering this e-mail to the intended recipient, any disclosure of this information in any way or taking of any action in reliance on this information is strictly prohibited. If you have received this e-mail in error, please notify the person transmitting the information

immediately.

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 **20170612172119198.pdf**
475K



Chemours™

The Chemours Company
Fluoroproducts
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

910-483-4681
chemours.com

CERTIFIED MAIL ARTICLE NUMBER 7002 0860 0006 9104 7828
RETURN RECEIPT REQUESTED

April 27, 2016

Ms. Wren Thedford
NCDEQ Division of Water Resources
NPDES Unit
1617 Mail Service Center
Raleigh, North Carolina 27699-1617

RECEIVED/NCDEQ/DWR

MAY 03 2016

SUBJECT: NPDES Permit Renewal Application
NPDES Permit No. NC0003573

Water Quality
Permitting Section

Dear Ms. Thedford:

The Chemours Company – Fayetteville Works is requesting renewal of NPDES Wastewater Discharge Permit No. NC0003573. Since the issuance of the last permit, the ownership of this facility changed from the DuPont Company to The Chemours Company FC, LLC. Also, two separate companies, Kuraray America Inc. and the DuPont Company, are operating manufacturing units and are treating and discharging their wastewaters under the Chemours' NPDES Permit.

Enclosed are the original and two copies of the General Information Form 1 (Form 3510-1), Wastewater Discharge Information Form 2C (Form 3510-2C), and additional required supporting documentation for renewal of the subject permit by the NC Division of Water Resources.

Included in the permit application are the following supplemental information documents: Sludge Management Plan, Current Facility Wastewater Management, Current Facility Operating Conditions, Alternate Application Schedule for §316(b) of the Clean Water Act, Elimination of Monitoring Requirement for PFOA, and the non-reporting of bis(chloromethyl) ether.

If you have any questions or need additional information, please contact me at (910) 678-1155.

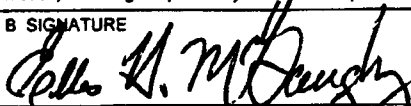
Sincerely,

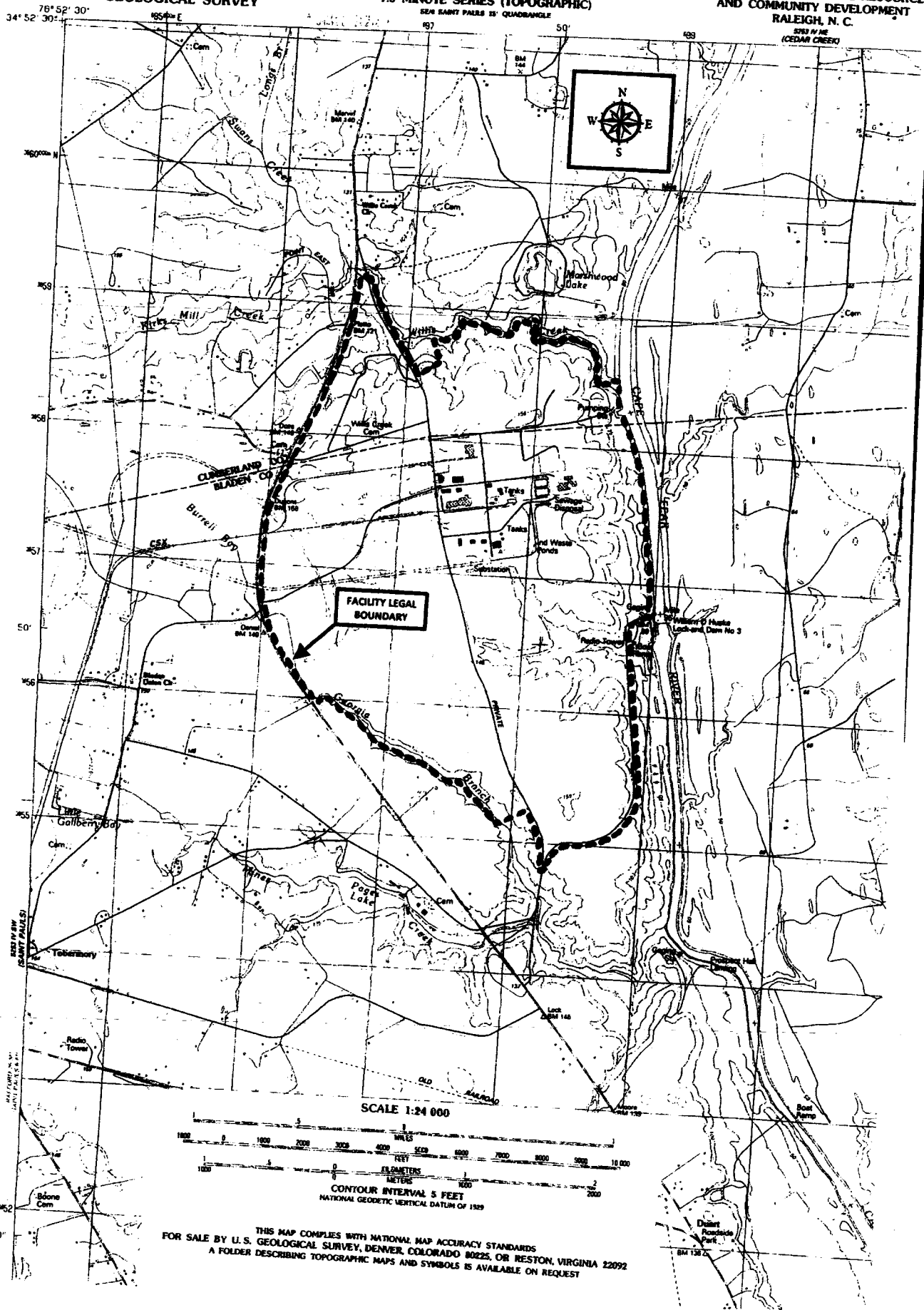
Michael E. Johnson, PE
Environmental Manager

Enclosures

CONTINUE ON REVERSE

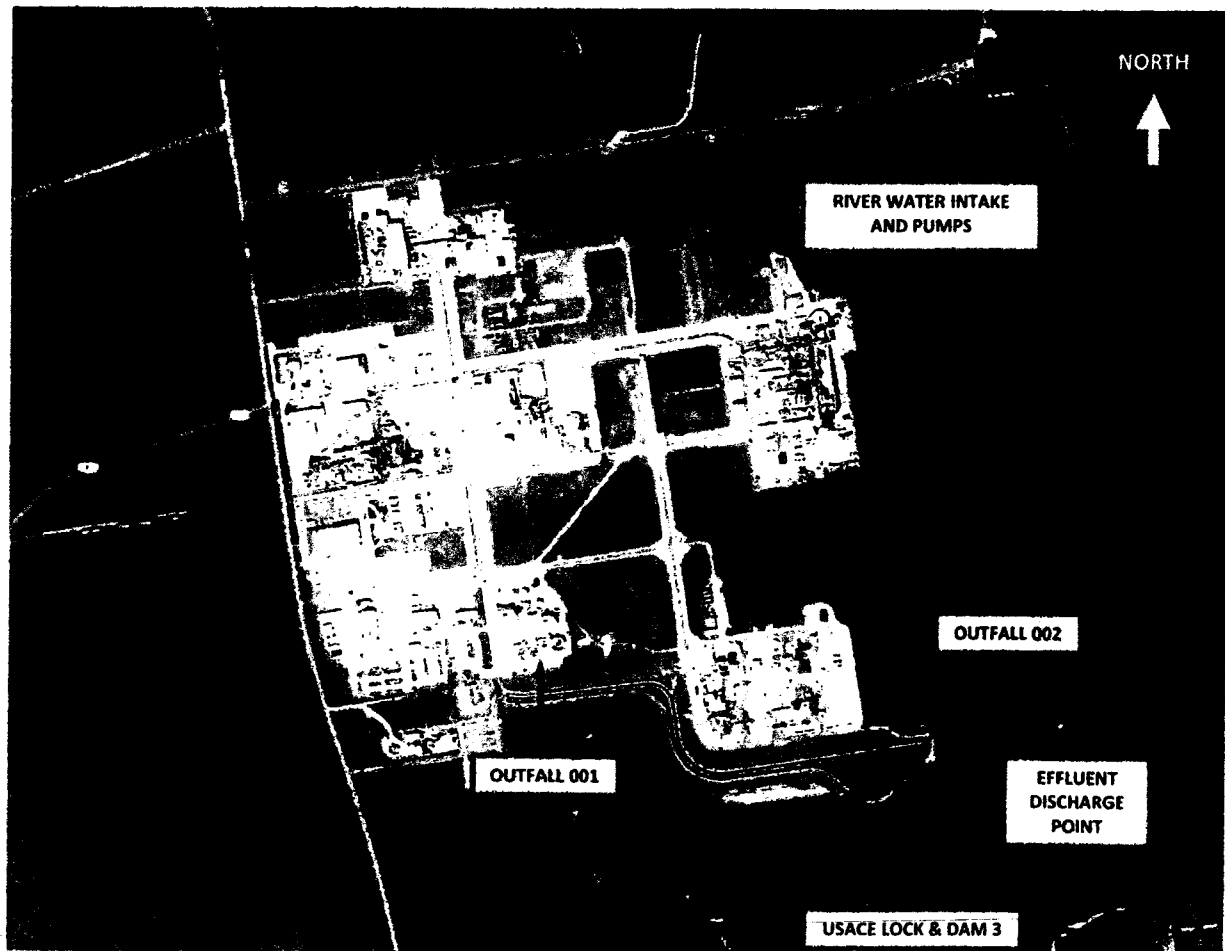
CONTINUED FROM THE FRONT

VII SIC CODES (4-digit, in order of priority)									
A FIRST					B SECOND				
C	7	2869	(specify) INDUSTRIAL ORGANIC CHEMICALS		C	7	3083	(specify) LAMINATED PLASTICS PLATE, SHEET, AND PROFILE SHAPES	
15	16	17	18	19	15	16	17	18	19
C THIRD					D FOURTH				
C	7	3081	(specify) UNSUPPORTED PLASTICS FILM AND SHEET NOTE: Kuraray Butacite Butacite® and SentryGlas® sheeting process units		C	7	2821	(specify) PLASTIC MATERIALS AND RESINS NOTE: DuPont PVF resin process units	
15	16	17	18	19	15	16	17	18	19
VIII OPERATOR INFORMATION									
A NAME								B. Is the name listed in item VIII-A also the owner?	
C	8	The Chemours Company FC, LLC							<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
15	16								15 16 17 18 19 20 21 22 23
C. STATUS OF OPERATOR (Enter the appropriate letter into the answer box if "Other," specify)								D PHONE (area code & no)	
F = FEDERAL		M = PUBLIC (other than federal or state)		P (specify)				A (302) 773-1000	
S = STATE		O = OTHER (specify)							
P = PRIVATE									
E STREET OR P.O. BOX									
1007 Market Street									
F CITY OR TOWN									
C	B	Wilmington							
15	16								40 41 42 43 44 45 46 47 48 49
G STATE					H ZIP CODE		IX INDIAN LAND		
DE					19898		Is the facility located on Indian lands? <input type="checkbox"/> YES <input checked="" type="checkbox"/> NO		
X EXISTING ENVIRONMENTAL PERMITS									
A NPDES (Discharges to Surface Water)					D PSD (Air Emissions from Proposed Sources)				
C	T	I			C	T	I		
9	N		NC0003573		9	P		NC Title V Permit 03735	
15	16	17	18	19	30	15	16	17	18
B UIC (Underground Injection of Fluids)					E OTHER (specify)				
C	T	I			C	T	I		
9	U		N/A		9			WQ0035431 (specify) Land Application Permit	
15	16	17	18	19	30	15	16	17	18
C RCRA (Hazardous Wastes)					E OTHER (specify)				
C	T	I			C	T	I		
9	R		NCD047368642		9			(specify)	
15	16	17	18	19	30	15	16	17	18
XI MAP									
Attach to this application a topographic map of the area extending to at least one mile beyond property boundaries. The map must show the outline of the facility, the location of each of its existing and proposed intake and discharge structures, each of its hazardous waste treatment, storage, or disposal facilities, and each well where it injects fluids underground. Include all springs, rivers, and other surface water bodies in the map area. See instructions for precise requirements.									
XII. NATURE OF BUSINESS (provide a brief description)									
The Chemours Company - Fayetteville Works (formerly the DuPont Company - Fayetteville Works) is a fluorinated chemicals manufacturer situated on a 2,200-acre property in northwestern Bladen County, NC.									
The Chemours' products produced at the facility include fluorinated monomers and fluorinated vinyl ethers, Nafion™ membranes and dispersion, and fluoropolymer processing aids. Chemours operates two natural gas / fuel oil-fired boilers, which provides steam for the entire facility.									
Also located at this facility are two tenant companies: Kuraray America Inc. and the DuPont Company. Kuraray operates the Butacite® polyvinyl butyral (PVB) thermoplastic sheet and resin manufacturing unit and the SentryGlas® ionoplast interlayer manufacturing unit. DuPont operates two polyvinyl fluoride (PVF) resin manufacturing units.									
Chemours receives and treats all of the Kuraray and DuPont process wastewater, sanitary wastewater, and contact stormwater in the Chemours' owned and operated wastewater treatment plant, and discharges that treated wastewater through Outfall 001 under the Chemours' NPDES Wastewater Discharge Permit (Permit No. NC0003573). The Kuraray and DuPont non-contact cooling waters and stormwaters are discharged through Outfall 002 under the Chemours' NPDES Wastewater Discharge Permit.									
XIII CERTIFICATION (see instructions)									
I certify under penalty of law that I have personally examined and am familiar with the information submitted in this application and all attachments and that, based on my inquiry of those persons immediately responsible for obtaining the information contained in the application, I believe that the information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment.									
A. NAME & OFFICIAL TITLE (type or print)					B SIGNATURE			C DATE SIGNED	
Ellis H. McGaughy - Plant Manager								4/27/2016	
COMMENTS FOR OFFICIAL USE ONLY									
C									
C									
15	16								15 16 17 18 19 20 21 22 23

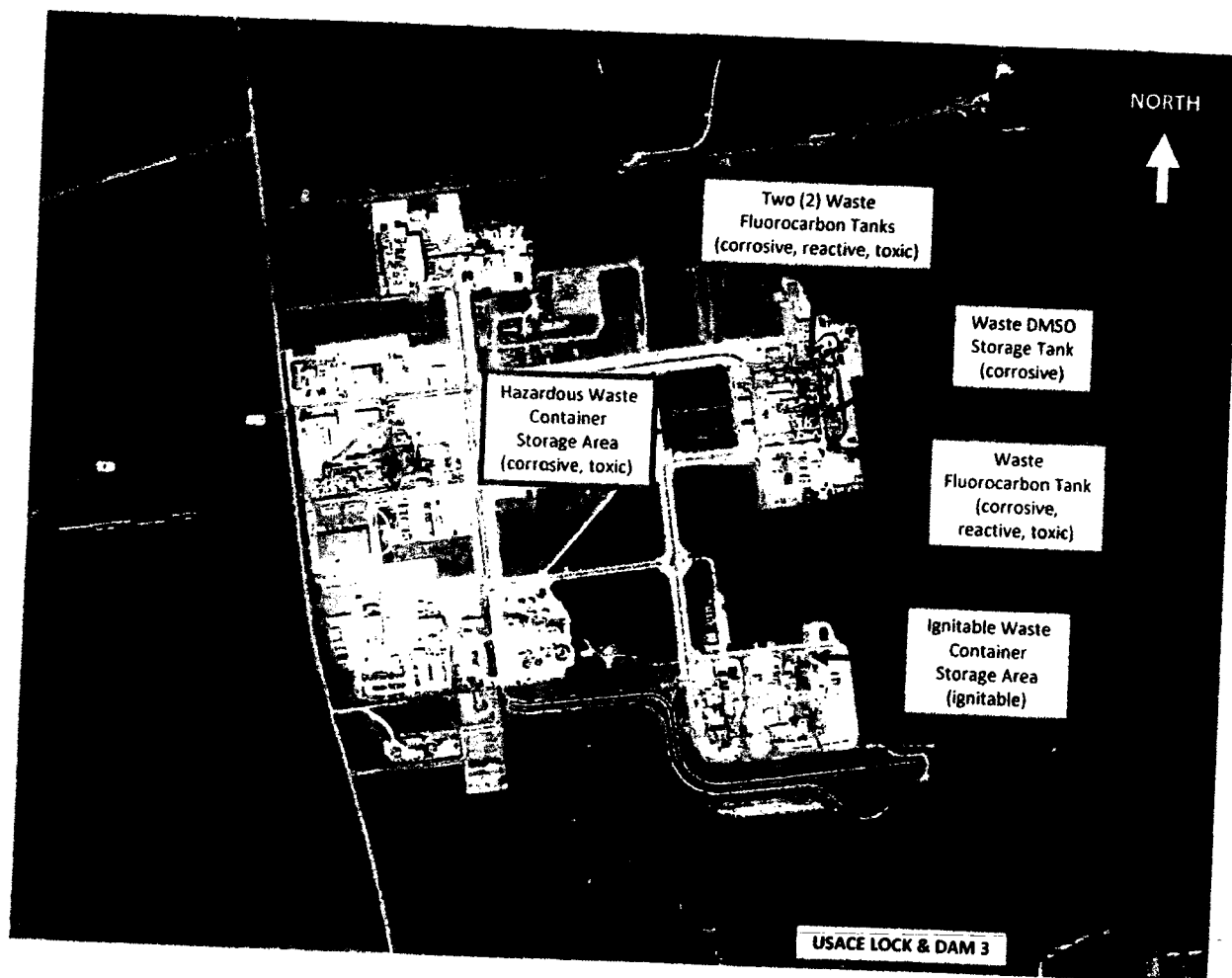


THIS MAP COMPLIES WITH NATIONAL MAP ACCURACY STANDARDS
FOR SALE BY U.S. GEOLOGICAL SURVEY, DENVER, COLORADO 80225, OR RESTON, VIRGINIA 22092
A FOLDER DESCRIBING TOPOGRAPHIC MAPS AND SYMBOLS IS AVAILABLE ON REQUEST

**CHEMOURS COMPANY – FAYETTEVILLE WORKS
LOCATIONS OF INTAKE AND DISCHARGE STRUCTURES**



CHEMOURS COMPANY – FAYETTEVILLE WORKS
LOCATIONS OF HAZARDOUS WASTE MANAGEMENT FACILITIES



Please print or type in the unshaded areas only.

EPA ID NUMBER (copy from Item 1 of Form 1)

NCD 047 368 642

Form Approved.
OMB No. 2040-0086
Approval expires 3-31-98

FORM
2C
NPDES



U.S. ENVIRONMENTAL PROTECTION AGENCY
APPLICATION FOR PERMIT TO DISCHARGE WASTEWATER
EXISTING MANUFACTURING, COMMERCIAL, MINING AND SILVICULTURE OPERATIONS
Consolidated Permits Program

I. OUTFALL LOCATION

For each outfall, list the latitude and longitude of its location to the nearest 15 seconds and the name of the receiving water.

A. OUTFALL NUMBER (/hr)	B. LATITUDE			C. LONGITUDE			D. RECEIVING WATER (name)
	1 DEG	2 MIN	3 SEC	1 DEG	2 MIN	3 SEC	
001	34.00	50.00	22.93	-78.00	50.00	11.47	Cape Fear River
002	34.00	50.00	21.58	-78.00	49.00	25.70	Cape Fear River

II. FLOWS, SOURCES OF POLLUTION, AND TREATMENT TECHNOLOGIES

A. Attach a line drawing showing the water flow through the facility. Indicate sources of intake water, operations contributing wastewater to the effluent, and treatment units labeled to correspond to the more detailed descriptions in Item B. Construct a water balance on the line drawing by showing average flows between intakes, operations treatment units, and outfalls. If a water balance cannot be determined (e.g., for certain mining activities), provide a pictorial description of the nature and amount of any sources of water and any collection or treatment measures.

B. For each outfall, provide a description of: (1) All operations contributing wastewater to the effluent, including process wastewater, sanitary wastewater, cooling water, and storm water runoff; (2) The average flow contributed by each operation; and (3) The treatment received by the wastewater. Continue on additional sheets if necessary.

1. OUTFALL NO. (/hr)	2. OPERATION(S) CONTRIBUTING FLOW		3. TREATMENT	
	a. OPERATION (/hr)	b. AVERAGE FLOW (include units)	a. DESCRIPTION	b. LIST CODES FROM TABLE 2C-1
001	Chemical Manufacturing Processes	159,361 gal/day	BIOLOGICAL WASTEWATER TREATMENT PLANT	
	Antaray Butarite Mfg Process	655,657 gal/day	(1) Influent Sump	1 C
	Antaray Sentry/Glas Mfg Process	0 gal/day	(2) Equalization with mixing and aeration	1 C 3 E
	Pulcont PVP Mfg Processes	211,654 gal/day	(3) Emergency Retention Tank	1 C
	Domestic water Neutralized Regenerate	75,000 gal/day	(4) Pre-Digester Tank	3 E
	Sanitary Sewer	10,000 gal/day	(5) Activated Sludge Aeration Tank	3 A
	Process Areas Stormwater	94,216 gal/day	(6) Clarification (3 clarifiers in parallel)	1 J
	TOTAL INFLUENT TO WWTP	1,205,888 gal/day		
	Evaporation from WWTP Operations	50,000 gal/day	BIOLOGICAL SLUDGE (SOLIDS) MANAGEMENT	
	Evaporation from Sludge Drying	19,943 gal/day	(1) Dissolved Air Flotation	5 J
002	Water Content of Landfilled Sludge	2,493 gal/day	(2) Rotary Filter	5 C
	OUTFALL 001 TOTAL EFFLUENT	1,133,452 gal/day	(3) Sludge Filter Press	1 R
			(4) Sludge Screen-Beared Driers	5 E
			(5) Disposal at Off-site Landfill	5 G
	Outfall 001 Treated Effluent	1,133,452 gal/day		
	Non Contact River Water	27,067,845 gal/day		
	Non contact filtered water	1,923,308 gal/day		
	Stormwater	211,503 gal/day		
	Sediment Removal	50,000 gal/day		
	Boiler Condensate Blowdown	321,000 gal/day		
003	OUTFALL 002 TOTAL EFFLUENT	16,812,133 gal/day	Discharge to surface water (Cape Fear River)	4 A

OFFICIAL USE ONLY (effluent guidelines sub-categories)

CONTINUED FROM THE FRONT

C Except for storm runoff, leaks, or spills, are any of the discharges described in Items II-A or B intermittent or seasonal?

☐ YES (complete the following table)

☒ NO (go to Section III)

1 OUTFALL NUMBER (list)	2 OPERATION(S) CONTRIBUTING FLOW (list)	3 FREQUENCY		4 FLOW					
		a DAYS PER WEEK (specify average)	b MONTHS PER YEAR (specify average)	a FLOW RATE (in mgd)		B TOTAL VOLUME (specify with units)		C DURATION (in days)	
				1 LONG TERM AVERAGE	2 MAXIMUM DAILY	1 LONG TERM AVERAGE	2 MAXIMUM DAILY		

III. PRODUCTION

A Does an effluent guideline limitation promulgated by EPA under Section 304 of the Clean Water Act apply to your facility?

☒ YES (complete Item III-B)

☐ NO (go to Section IV)

B Are the limitations in the applicable effluent guideline expressed in terms of production (or other measure of operation)?

☐ YES (complete Item III-C)

☒ NO (go to Section IV)

C If you answered "yes" to Item III-B, list the quantity which represents an actual measurement of your level of production, expressed in the terms and units used in the applicable effluent guideline, and indicate the affected outfalls.

1. AVERAGE DAILY PRODUCTION			2. AFFECTED OUTFALLS (list outfall numbers)
a QUANTITY PER DAY	b UNITS OF MEASURE	c OPERATION, PRODUCT, MATERIAL, ETC. (specify)	

IV. IMPROVEMENTS

A Are you now required by any Federal, State or local authority to meet any implementation schedule for the construction, upgrading or operations of wastewater treatment equipment or practices or any other environmental programs which may affect the discharges described in this application? This includes, but is not limited to, permit conditions, administrative or enforcement orders, enforcement compliance schedule letters, stipulations, court orders, and grant or loan conditions

☐ YES (complete the following table)

☒ NO (go to Item IV-B)

1 IDENTIFICATION OF CONDITION AGREEMENT, ETC.	2 AFFECTED OUTFALLS		3 BRIEF DESCRIPTION OF PROJECT	4 FINAL COMPLIANCE DATE	
	a NO	b SOURCE OF DISCHARGE		a REQUIRED	b PROJECTED

B OPTIONAL: You may attach additional sheets describing any additional water pollution control programs (or other environmental projects which may affect your discharges) you now have underway or which you plan. Indicate whether each program is now underway or planned and indicate your actual or planned schedules for construction

☐ MARK "X" IF DESCRIPTION OF ADDITIONAL CONTROL PROGRAMS IS ATTACHED

A, B & C See instructions before proceeding – Complete one set of tables for each outfall – Annotate the outfall number in the space provided
NOTE: Tables V-A, V-B, and V-C are included on separate sheets numbered V-1 through V-9.

<p> 1. POLLUTANT 2 SOURCE 1. POLLUTANT 2. SOURCE </p>			
<p> None of the pollutants listed in Table 2C-3 are believed to be present in the wastewater discharge from this site. </p>			

Is any pollutant listed in Item V-C a substance or a component of a substance which you currently use or manufacture as an intermediate or final product or byproduct?

☒ YES (list all such pollutants below) ☐ NO (go to Item VI-B)

Antimony
Benzene
1,2-dichloroethane
Methylene chloride
Toluene

CONTINUED FROM THE FRONT

VII. BIOLOGICAL TOXICITY TESTING DATA

Do you have any knowledge or reason to believe that any biological test for acute or chronic toxicity has been made on any of your discharges or on a receiving water in relation to your discharge within the last 3 years?

☒ YES (Identify the test(s) and describe their purposes below)

☐ NO (go to Section VIII)

The "North Carolina Ceriodaphnia Chronic Effluent Bioassay Procedure" is performed each quarter in accordance with the requirement of condition A(4) of the facility's NPDES Permit. The NCDEQ Division of Water Resources has copies of the Form AT-1 test results that were submitted with the Discharge Monitoring Reports during the period from February 2012 through February 2016.

The quarterly chronic test performed during February 2012, failed for the ceriodaphnia dubia reproduction. The required monthly chronic tests performed in March and April 2012 both passed. No other toxicity test failures occurred during the five-year term of the current permit.

VIII. CONTRACT ANALYSIS INFORMATION

Were any of the analyses reported in Item V performed by a contract laboratory or consulting firm?

☒ YES (list the name, address and telephone number of, and pollutants analyzed by, each such laboratory or firm below)

☐ NO (go to Section IX)

A NAME	B ADDRESS	C TELEPHONE (area code & no)	D. POLLUTANTS ANALYZED (list)
TBL	2401 West 5th Street Lumberton, NC 28358	910-738-6190	Chemical Oxygen Demand (COD); Total Organic Carbon (TOC); Total Suspended Solids (TSS); Ammonia (as N); Color; Fecal Coliform; Fluoride; Nitrate-Nitrite (as N); Nitrogen; Total Organic (as N); Oil and Grease; Total Phosphorus (as P); Sulfate (as SO4); Surfactants; Total Aluminum; Total Iron; Total Magnesium; Total Manganese; Part C Metals, Cyanide, and Total Phenols; Part C GC/MS - Volatile Compounds; Part C GC/MS - Acid Compounds; Part C GC/MS - Base/Neutral Compounds; Part C GC/MS Fraction - Pesticides

IX. CERTIFICATION

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

A NAME & OFFICIAL TITLE (type or print)

Ellis H. McGaughy - Plant Manager

B PHONE NO. (area code & no)

(910) 678-1224

C SIGNATURE

Ellis H. McGaughy

D DATE SIGNED

04/27/2016

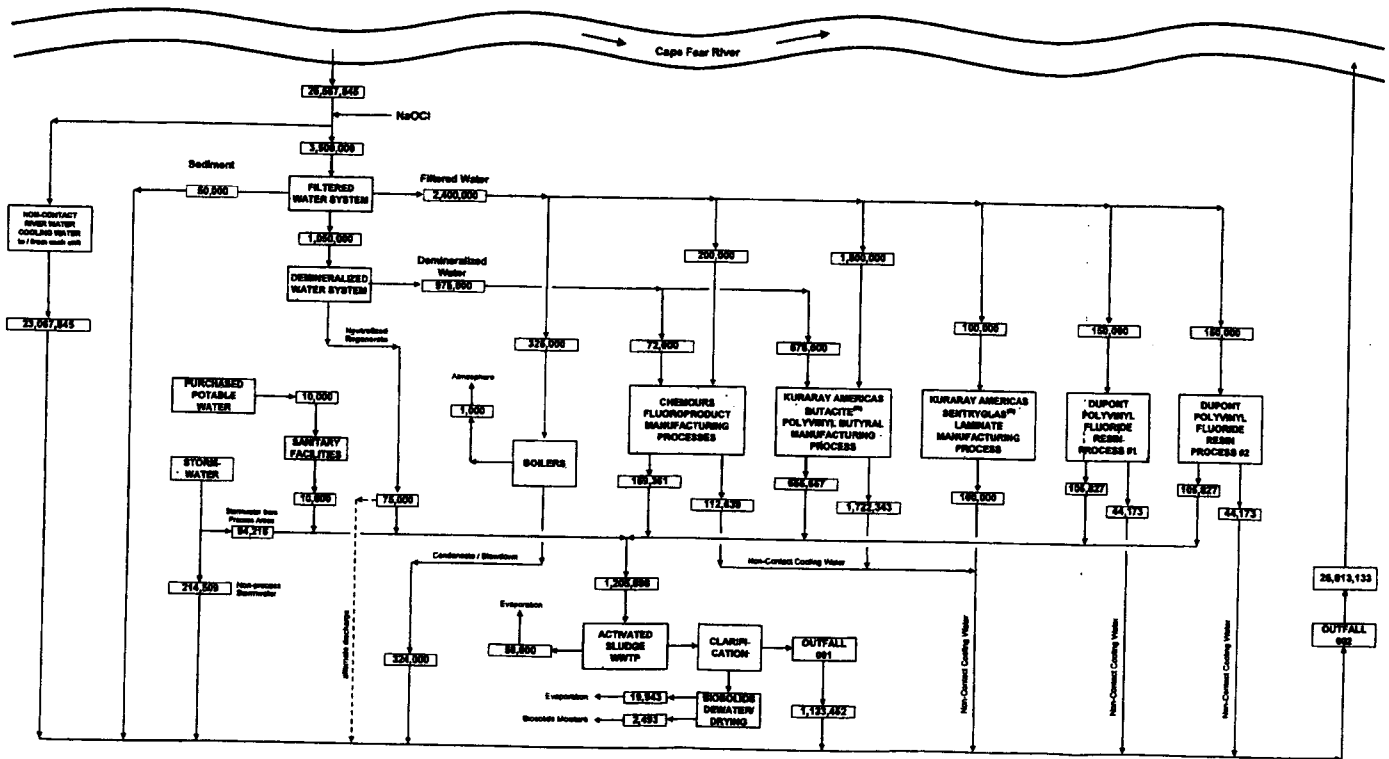
FORM 2C ITEM 8-A: LINE DRAWING

WATER BALANCE (Revised 04-21-2016)

Flow Units: Gallons per Day

Base: (1) All Manufacturing Units operating
(2) Maximum 30-day average of measured flows (2013 - 2015)

NPDES PERMIT RENEWAL APPLICATION
Chemours Company - Fayetteville Works
NPDES Permit No. NC0003673



OUTFALL 001

PLEASE PRINT OR TYPE IN THE UNSHADED AREAS ONLY. You may report some or all of this information on separate sheets (use the same format) instead of completing these pages. SEE INSTRUCTIONS.

EPA I.D. NUMBER (copy from Item 1 of Form 1)
NCD 047 368 642

V. INTAKE AND EFFLUENT CHARACTERISTICS (continued from page 3 of Form 2-C)												OUTFALL NO. 001	
PART A -- You must provide the results of at least one analysis for every pollutant in this table. Complete one table for each outfall. See instructions for additional details.													
1. POLLUTANT	2. EFFLUENT						d. NO. OF ANALYSES	3. UNITS (specify if blank)		4. INTAKE (optional)			
	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)			a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES	
	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS		
a. Biochemical Oxygen Demand (BOD)	71.0	675.9	26.8	207.1	5.8	37.8	465	mg/L	lb.	n/a	n/a	n/a	
b. Chemical Oxygen Demand (COD)	32.1	313.2					1	mg/L	lb.	n/a	n/a	n/a	
c. Total Organic Carbon (TOC)	84.9	828.4					1	mg/L	lb.	n/a	n/a	n/a	
d. Total Suspended Solids (TSS)	44.0	387.8	22.0	177.0	9.8	54.6	465	mg/L	lb.	n/a	n/a	n/a	
e. Ammonia (as N)	0.414	4.0					1	mg/L	lb.	n/a	n/a	n/a	
f. Flow	VALUE 1.627		VALUE 1.133		VALUE 0.907		1095	MGD	MGD	VALUE n/a		n/a	
g. Temperature (winter)	VALUE 26.0		VALUE 22.2		VALUE 18.4		118	°C		VALUE n/a		n/a	
h. Temperature (summer)	VALUE 32.0		VALUE 30.6		VALUE 29.0		118	°C		VALUE n/a		n/a	
i. pH	MINIMUM 6.37	MAXIMUM 8.47	MINIMUM n/a	MAXIMUM n/a			374	STANDARD UNITS					

PART B -- Mark "X" in column 2-a for each pollutant you know or have reason to believe is present. Mark "X" in column 2-b for each pollutant you believe to be absent. If you mark column 2a for any pollutant which is limited either directly, or indirectly but expressly, in an effluent limitations guideline, you must provide the results of at least one analysis for that pollutant. For other pollutants for which you mark column 2a, you must provide quantitative data or an explanation of their presence in your discharge. Complete one table for each outfall. See the instructions for additional details and requirements.

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT						4. UNITS		5. INTAKE (optional)			
	a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
a. Bromide (24959-67-9)		X												
b. Chlorine, Total Residual	X		0.03	0.3					1	mg/L	lb.	n/a	n/a	
c. Color	X		10	n/a					1	PCU	n/a	n/a	n/a	
d. Fecal Coliform	X		est. 2	n/a					1	col/dL	n/a	n/a	n/a	
e. Fluoride (10694-48-5)	X		170	1659					1	mg/L	lb.	n/a	n/a	
f. Nitrate-Nitrite (as N)	X		0.065	0.6					1	mg/L	lb.	n/a	n/a	

OUTFALL 001

ITEM V-8 CONTINUED FROM FRONT

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT						4. NO. OF ANALYSES	4. UNITS		5. INTAKE (optional)		
	a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)			a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
g. Nitrogen, Total Organic (or N)	X		1.016	9.9					1	mg/L	lb.	n/a	n/a	n/a
h. Oil and Grease	X		<5.6	<50.0	5.2	42.5	0.26	1.87	36	mg/L	lb.	n/a	n/a	n/a
i. Phosphorus (as P), Total (7723-14-0)	X		12.4	121.0					1	mg/L	lb.	n/a	n/a	n/a
j. Radioactivity														
(1) Alpha, Total		X												
(2) Beta, Total		X												
(3) Radium, Total		X												
(4) Radium 226, Total		X												
k. Sulfate (as SO ₄) (14808-79-8)	X		1083	10568					1	mg/L	lb.	n/a	n/a	n/a
l. Sulfide (as S)		X												
m. Sulfite (as SO ₃) (14265-45-3)		X												
n. Surfactants	X		3.07	30.0										
o. Aluminum, Total (7429-90-5)	X		0.19	1.9					1	mg/L	lb.	n/a	n/a	n/a
p. Barium, Total (7440-39-3)		X							1	mg/L	lb.	n/a	n/a	n/a
q. Boron, Total (7440-42-8)		X												
r. Cobalt, Total (7440-48-4)		X												
s. Iron, Total (7439-89-6)	X		0.28	2.7										
t. Magnesium, Total (7439-95-4)	X		2.26	22.1					1	mg/L	lb.	n/a	n/a	n/a
u. Molybdenum, Total (7439-98-7)		X							1	mg/L	lb.	n/a	n/a	n/a
v. Manganese, Total (7439-96-5)	X		<0.005	<0.049										
w. Tin, Total (7440-31-6)		X							1	mg/L	lb.	n/a	n/a	n/a
x. Titanium, Total (7440-32-6)		X												

OUTFALL 001

EPA I.D. NUMBER (copy from Item 1 of Form 1)
NCD 047 368 642OUTFALL NUMBER
001

CONTINUED FROM PAGE 3 OF FORM 2-C

PART C - If you are a primary industry and this outfall contains process wastewater, refer to Table 2b-2 in the instructions to determine which of the GC/MS fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2-a (secondary industries, nonprocess wastewater outfalls, and nonrequired GC/MS fractions), mark "X" in column 2-b for each pollutant you know or have reason to believe is present. Mark "X" in column 2-c for each pollutant you believe is absent. If you mark column 2a for any pollutant, you must provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for that pollutant if you know or have reason to believe it will be discharged in concentrations of 10 ppb or greater. If you mark column 2b for acrolein, acrylonitrile, 2,4 dinitrophenol, or 2-methyl-4, 6 dinitrophenol, you must provide the results of at least one analysis for each of these pollutants which you know or have reason to believe that you discharge in concentrations of 100 ppb or greater. Otherwise, for pollutants for which you mark column 2b, you must either submit at least one analysis or briefly describe the reasons the pollutant is expected to be discharged. Note that there are 7 pages to this part, please review each carefully. Complete one table (all 7 pages) for each outfall. See instructions for additional details and requirements.

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS		5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	e. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS		
																(1) CONCENTRATION
METALS, CYANIDE, AND TOTAL PHENOLS																
1M. Antimony, Total (7440-38-0)	X			<0.002	<0.020					1	mg/L	lb.	n/a	n/a	n/a	
2M. Arsenic, Total (7440-38-2)	X			<0.005	<0.049					1	mg/L	lb.	n/a	n/a	n/a	
3M. Beryllium, Total (7440-41-7)	X			<0.001	<0.010					1	mg/L	lb.	n/a	n/a	n/a	
4M. Cadmium, Total (7440-43-8)	X			<0.002	<0.020					1	mg/L	lb.	n/a	n/a	n/a	
5M. Chromium, Total (7440-47-3)	X			0.010	0.070	0.010	0.070	0.004	0.034	4	mg/L	lb.	n/a	n/a	n/a	
6M. Copper, Total (7440-50-8)	X			0.007	0.050	0.007	0.050	0.0055	0.047	4	mg/L	lb.	n/a	n/a	n/a	
7M. Lead, Total (7439-92-1)	X			<0.003	<0.029					1	mg/L	lb.	n/a	n/a	n/a	
8M. Mercury, Total (7439-97-6)	X			<0.0002	<0.002					1	mg/L	lb.	n/a	n/a	n/a	
9M. Nickel, Total (7440-02-0)	X			0.012	0.090	0.012	0.090	0.0083	0.065	4	mg/L	lb.	n/a	n/a	n/a	
10M. Selenium, Total (7782-49-2)	X			<0.005	<0.049					1	mg/L	lb.	n/a	n/a	n/a	
11M. Silver, Total (7440-22-4)	X			<0.002	<0.020					1	mg/L	lb.	n/a	n/a	n/a	
12M. Thallium, Total (7440-28-0)	X			<0.005	<0.049					1	mg/L	lb.	n/a	n/a	n/a	
13M. Zinc, Total (7440-66-6)	X			0.042	0.390	0.042	0.390	0.0343	0.286	4	mg/L	lb.	n/a	n/a	n/a	
14M. Cyanide, Total (57-12-5)	X			<0.005	<0.049					1	mg/L	lb.	n/a	n/a	n/a	
15M. Phenols, Total	X			<0.0400	<0.390					1	mg/L	lb.	n/a	n/a	n/a	
DIOXIN																
2,3,7,8-Tetrachlorodibenzo-P-Dioxin (1784-01-6)			X	DESCRIBE RESULTS Not applicable												

OUTFALL 001

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS			5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	e. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES		
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS			
GC/MS FRACTION - VOLATILE COMPOUNDS																	
1V. Acetone (107-02-8)	X			<0.0500	<0.488					1	mg/L	lb.	n/a	n/a	n/a		
2V. Acrylonitrile (107-13-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
3V. Benzene (71-43-2)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
4V. Bis (Chloromethyl) Ether (542-88-1)			X	Not Req	ired	per NCDWR	NPDES	Permitt'g	Unit								
5V. Bromoform (75-25-2)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
6V. Carbon Tetrachloride (56-23-5)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
7V. Chlorobenzene (108-90-7)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
8V. Chlorodibromomethane (124-48-1)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
9V. Chloroethane (75-00-3)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
10V. 2-Chloroethylvinyl Ether (110-75-8)	X			<0.0500	<0.488					1	mg/L	lb.	n/a	n/a	n/a		
11V. Chloroform (67-68-3)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
12V. Dichlorobromomethane (75-27-4)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
13V. Dichlorodifluoromethane (75-71-8)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
14V. 1,1-Dichloroethane (75-34-3)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
15V. 1,2-Dichloroethane (107-06-2)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
16V. 1,1-Dichloroethylene (75-35-4)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
17V. 1,2-Dichloropropane (78-87-5)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
18V. 1,3-Dichloropropylene (542-75-6)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
19V. Ethylbenzene (100-41-4)	X			<0.00100	<0.10					1	mg/L	lb.	n/a	n/a	n/a		
20V. Methyl Bromide (74-83-9)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
21V. Methyl Chloride (74-87-3)	X			<0.00250	<0.024					1	mg/L	lb.	n/a	n/a	n/a		

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CONTINUED FROM PAGE V-4

1 POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS			5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	e. CONCENTRATION	f. MASS	g. LONG TERM AVERAGE VALUE		h. NO. OF ANALYSES		
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS			
GC/MS FRACTION - VOLATILE COMPOUNDS (continued)																	
22V. Methylene Chloride (75-09-2)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
23V. 1,1,2,2-Tetrachloroethane (79-34-5)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
24V. Tetrachloroethylene (127-18-4)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
25V. Toluene (108-88-3)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
26V. 1,2-Trans-Dichloroethylene (156-60-5)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
27V. 1,1,1-Trichloroethane (71-55-6)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
28V. 1,1,2-Trichloroethane (79-00-5)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
29V. Trichloroethylene (79-01-6)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
30V. Trichlorofluoromethane (75-69-4)	X			<0.00500	<0.049					1	mg/L	lb.	n/a	n/a	n/a		
31V. Vinyl Chloride (75-01-4)	X			<0.00100	<0.010					1	mg/L	lb.	n/a	n/a	n/a		
GC/MS FRACTION - ACID COMPOUNDS																	
1A. 2-Chlorophenol (95-57-8)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
2A. 2,4-Dichlorophenol (120-83-2)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
3A. 2,4-Dimethylphenol (105-67-9)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
4A. 4,6-Dinitro-O-Cresol (534-52-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
5A. 2,4-Dinitrophenol (51-28-5)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
6A. 2-Nitrophenol (88-75-5)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
7A. 4-Nitrophenol (100-02-7)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
8A. P-Chloro-M-Cresol (58-50-7)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
9A. Pentachlorophenol (87-86-5)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
10A. Phenol (108-95-2)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
11A. 2,4,6-Trichlorophenol (88-05-2)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
EPA Form 3510-2C (8-90)																	

OUTFALL 001

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS		5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS		
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS																
18. Acenaphthene (83-32-9)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
28. Acenaphthylene (208-96-8)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
38. Anthracene (120-12-7)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
48. Benzidine (92-87-5)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
58. Benzo (a) Anthracene (56-55-3)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
68. Benzo (a) Pyrene (50-32-6)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
78. 3,4-Benzo-fluoranthene (205-99-2)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
88. Benzo (ghi) Perylene (191-24-2)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
98. Benzo (h) Fluoranthene (207-06-8)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
108. Bis (2-Chloro-octyl) Methane (111-91-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
118. Bis (2-Chloro-octyl) Ether (111-44-4)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
128. Bis (2-Chlorooctadecyl) Ether (102-90-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
138. Bis (2-Ethylhexyl) Phthalate (117-81-7)	X			<0.00300	<0.029					1	mg/L	lb.	n/a	n/a	n/a	
148. 4-Bromophenyl Phenyl Ether (101-55-3)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
158. Butyl Benzyl Phthalate (85-88-7)	X			<0.00300	<0.029					1	mg/L	lb.	n/a	n/a	n/a	
168. 2-Chloronaphthalene (91-58-7)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
178. 4-Chlorophenyl Phenyl Ether (7005-72-3)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
188. Chrysene (218-01-6)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
198. Dibenzo (a,h) Anthracene (53-70-3)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
208. 1,2-Dichlorobenzene (95-50-1)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	
218. 1,3-Dichlorobenzene (541-73-1)	X			<0.00100	<0.01					1	mg/L	lb.	n/a	n/a	n/a	

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CONTINUED FROM PAGE V-6

CONTINUED FROM PAGE V-6																	
1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS			5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES		
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS			
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS (continued)																	
228. 1,4-Dichlorobenzene (106-46-7)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a		
238. 3,3-Dichlorobenzidine (91-94-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
248. Diethyl Phthalate (84-66-2)	X			<0.00300	<0.029					1	mg/L	lb.	n/a	n/a	n/a		
258. Dimethyl Phthalate (131-11-3)	X			<0.00300	<0.029					1	mg/L	lb.	n/a	n/a	n/a		
268. Di-N-Butyl Phthalate (84-74-2)	X			<0.00300	<0.029					1	mg/L	lb.	n/a	n/a	n/a		
278. 2,4-Dinitrotoluene (121-14-2)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
288. 2,6-Dinitrotoluene (806-20-2)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
298. Di-N-Octyl Phthalate (117-84-0)	X			<0.00300	<0.029					1	mg/L	lb.	n/a	n/a	n/a		
308. 1,2-Diphenylhydrazine (as Azo-benzene) (122-66-7)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
318. Fluoranthene (208-44-0)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a		
328. Fluorene (86-73-7)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a		
338. Hexachlorobenzene (118-74-1)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a		
348. Hexachlorobutadiene (87-68-3)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
358. Hexachlorocyclopentadiene (77-47-4)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
368. Hexachloroethane (67-72-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
378. Indeno (1,2,3-cd) Pyrene (183-39-5)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a		
388. Isophorone (78-59-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
398. Naphthalene (91-20-3)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a		
408. Nitrobenzene (98-95-3)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
418. N-Nitrosodimethylamine (52-75-9)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		
428. N-Nitrosodi-N-Propylamine (521-64-7)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a		

OUTFALL 001

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS		5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS		
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS (continued)																
43B. N-Nitrosodiphenylamine (88-30-6)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
44B. Phenanthrene (85-01-8)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a	
45B. Pyrene (129-00-0)	X			<0.00100	<0.001					1	mg/L	lb.	n/a	n/a	n/a	
46B. 1,2,4-Trichlorobenzene (120-82-1)	X			<0.0100	<0.098					1	mg/L	lb.	n/a	n/a	n/a	
GC/MS FRACTION - PESTICIDES																
1P. Aldrin (309-00-2)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
2P. α-BHC (319-84-6)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
3P. β-BHC (319-85-7)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
4P. γ-BHC (58-98-9)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
5P. δ-BHC (319-86-8)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
6P. Chlordane (57-74-9)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a	
7P. 4,4'-DDT (50-29-3)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
8P. 4,4'-DDE (72-55-8)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
9P. 4,4'-DDD (72-54-8)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
10P. Dieldrin (60-57-1)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
11P. α-Endosulfan (115-29-7)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
12P. β-Endosulfan (115-29-7)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
13P. Endosulfan Sulfate (1031-07-8)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
14P. Endrin (72-20-8)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
15P. Endrin Aldehyde (7421-83-4)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	
16P. Heptachlor (78-44-8)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a	

EPA Form 3510-2C (8-90)

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OUTFALL 001

CONTINUED FROM PAGE V-8		EPA ID. NUMBER (copy from Item 1 of Form 1)		OUTFALL NUMBER											
		NCD 047 368 642		001											
1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT						4. UNITS		5. INTAKE (optional)			
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	e. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
GC/MS FRACTION - PESTICIDES (continued)															
17P. Heptachlor Epoxide (1024-57-3)	X			<0.000050	<5e-4					1	mg/L	lb.	n/a	n/a	n/a
18P. PCB-1242 (53498-21-6)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
19P. PCB-1254 (11087-69-1)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
20P. PCB-1221 (11104-28-2)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
21P. PCB-1232 (11141-16-5)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
22P. PCB-1248 (12672-29-6)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
23P. PCB-1260 (11086-82-5)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
24P. PCB-1016 (12674-11-2)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a
25P. Toxaphene (8001-35-2)	X			<0.000500	<0.005					1	mg/L	lb.	n/a	n/a	n/a

OUTFALL 002

PLEASE PRINT OR TYPE IN THE UNSHADED AREAS ONLY. You may report some or all of this information on separate sheets (use the same format) instead of completing these pages.
SEE INSTRUCTIONS.

EPA I.D. NUMBER (copy from Item 1 of Form 1)
NCD 047 368 642

OUTFALL NO.
002

V. INTAKE AND EFFLUENT CHARACTERISTICS (continued from page 3 of Form 2-C)

PART A - You must provide the results of at least one analysis for every pollutant in this table. Complete one table for each outfall. See instructions for additional details.

1. POLLUTANT	2. EFFLUENT						3. UNITS (specify if blank)		4. INTAKE (optional)			
	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES
	(1)	(2)	(1)	(2)	(1)	(2)				(1)	(2)	
	CONCENTRATION	MASS	CONCENTRATION	MASS	CONCENTRATION	MASS				CONCENTRATION	MASS	
a. Biochemical Oxygen Demand (BOD)	3.9	762.1	3.9	762.1	1.4	185.7	12	mg/L	1b.	n/a	n/a	n/a
b. Chemical Oxygen Demand (COD)	33.7	4898	33.7	4898	4.37	458.6	12	mg/L	1b.	n/a	n/a	n/a
c. Total Organic Carbon (TOC)	12.8	1135					1	mg/L	1b.	n/a	n/a	n/a
d. Total Suspended Solids (TSS)	10.6	939.7					1	mg/L	1b.	n/a	n/a	n/a
e. Ammonia (as N)	0.410	36.3					1	mg/L	1b.	n/a	n/a	n/a
f. Flow	VALUE	34.791	VALUE	26.813	VALUE	14.556	1095	MGD	MGD	VALUE	n/a	n/a
g. Temperature (winter)	VALUE	22.0	VALUE	18.8	VALUE	14.1	188	°C		VALUE	n/a	n/a
h. Temperature (summer)	VALUE	33.0	VALUE	31.1	VALUE	30.0	190	°C		VALUE	n/a	n/a
i. pH	MINIMUM	6.11	MAXIMUM	8.16	MINIMUM	n/a	MAXIMUM	n/a		647	STANDARD UNITS	
PART B -- Mark "X" in column 2-4 for each pollutant you know or have access to in the effluent.												

PART B - Mark "X" in column 2-a for each pollutant you know or have reason to believe is present. Mark "X" in column 2-b for each pollutant you believe to be absent. If you mark column 2a for any pollutant which is limited either directly, or indirectly but expressly, in an effluent limitations guideline, you must provide the results of at least one analysis for that pollutant. For other pollutants for which you mark column 2a, you must provide quantitative data or an explanation of their presence in your discharge. Complete one table for each outfall. See the instructions for additional details and requirements.

1. POLLUTANT AND CAS NO. (if available)															2. MARK "X"		3. EFFLUENT								4. UNITS			5. INTAKE (optional)				
															a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	e. CONCENTRATION	f. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES				
																	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS					
a. Bromide (24859-87-9)																X																
b. Chlorine, Total Residual															X		0.14	12.4					1	mg/L	1b.	n/a	n/a	n/a				
c. Color															X		27	n/a					1	PCU	n/a	n/a	n/a	n/a				
d. Fecal Coliform															X		est. 2	n/a					1	col/dL	n/a	n/a	n/a	n/a				
e. Fluoride (16984-48-8)															X		35.1	4110	35.1	4110	17.3	1783	12	col/dL	n/a	n/a	n/a	n/a				
f. Nitrate-Nitrite (as N)															X		2.4	442.9	2.4	442.9	1.04	127.5	36	mg/L	1b.	n/a	n/a	n/a	n/a			
EPA Form 3510-2C (8-90)																								mg/L	1b.	n/a	n/a	n/a				

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ITEM V-B CONTINUED FROM FRONT

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT								4. UNITS		5. INTAKE (optional)		
	a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES	
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS		
g. Nitrogen, Total Organic (m N)	X		0.362	32.1					1	mg/L	lb.	n/a	n/a	n/a	
h. Oil and Grease	X		<4.76	<422					1	mg/L	lb.	n/a	n/a	n/a	
i. Phosphorus (as P), Total (7723-14-0)	X		1.2	154	1.2	154	0.8	85.8	36	mg/L	lb.	n/a	n/a	n/a	
j. Radioactivity															
(1) Alpha, Total		X													
(2) Beta, Total		X													
(3) Radium, Total		X													
(4) Radium 226, Total		X													
k. Sulfate (as SO ₄) (14808-79-8)	X		105	9309					1	mg/L	lb.	n/a	n/a	n/a	
l. Sulfide (as S)		X													
m. Sulfite (as SO ₃) (14265-45-3)		X													
n. Surfactants	X		0.552	48.9					1	mg/L	lb.	n/a	n/a	n/a	
o. Aluminum, Total (7429-90-5)	X		1.27	112.6					1	mg/L	lb.	n/a	n/a	n/a	
p. Barium, Total (7440-39-3)		X													
q. Boron, Total (7440-42-8)		X													
r. Cobalt, Total (7440-48-4)		X													
s. Iron, Total (7439-89-6)	X		1.15	102.0					1	mg/L	lb.	n/a	n/a	n/a	
t. Magnesium, Total (7439-95-4)	X		2.26	200.4					1	mg/L	lb.	n/a	n/a	n/a	
u. Molybdenum, Total (7439-98-7)		X													
v. Manganese, Total (7439-96-5)	X		0.069	6.12					1	mg/L	lb.	n/a	n/a	n/a	
w. Tin, Total (7440-31-5)		X													
x. Titanium, Total (7440-32-6)		X													

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NCD 047 368 642	002

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PART C - If you are a primary industry and this outfall contains process wastewater, refer to Table 2c-2 in the instructions to determine which of the GC/MS fractions you must test for. Mark "X" in column 2-a for all such GC/MS fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2-a (secondary industries, nonprocess wastewater outfalls, and nonregulated GC/MS fractions), mark "X" in column 2-b for each pollutant you know or have reason to believe is present. Mark "X" in column 2-c for each pollutant you believe is absent. If you mark column 2a for any pollutant, you must provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for that pollutant if you know or have reason to believe it will be discharged in concentrations of 10 ppb or greater. If you mark column 2b for acrolein, acrylonitrile, 2,4-dinitrophenol, or 2-methyl-4, 6-dinitrophenol, you must provide the results of at least one analysis for each of these pollutants which you know or have reason to believe that you discharge in concentrations of 100 ppb or greater. Otherwise, for pollutants for which you mark column 2b, you must either submit at least one analysis or briefly describe the reasons the pollutant is expected to be discharged. Note that there are 7 pages to this part, please review each carefully. Complete one table (all 7 pages) for each outfall. See instructions for additional details and requirements.

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT						4. UNITS		5. INTAKE (optional)			
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO OF ANALYSES
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
METALS, CYANIDE, AND TOTAL PHENOLS															
1M. Arsenic, Total (7440-36-0)	X			<0.002	<0.177					1	mg/L	1b.	n/a	n/a	n/a
2M. Arsenic, Total (7440-36-2)	X			<0.005	<0.443					1	mg/L	1b.	n/a	n/a	n/a
3M. Beryllium, Total (7440-41-7)	X			<0.001	<0.089					1	mg/L	1b.	n/a	n/a	n/a
4M. Cadmium, Total (7440-43-8)	X			<0.002	<0.177					1	mg/L	1b.	n/a	n/a	n/a
5M. Chromium, Total (7440-47-3)	X			<0.005	<0.433					1	mg/L	1b.	n/a	n/a	n/a
6M. Copper, Total (7440-50-8)	X			0.005	0.443					1	mg/L	1b.	n/a	n/a	n/a
7M. Lead, Total (7439-92-1)	X			<0.003	<0.266					1	mg/L	1b.	n/a	n/a	n/a
8M. Mercury, Total (7439-97-6)	X			<0.0002	<0.018					1	mg/L	1b.	n/a	n/a	n/a
9M. Nickel, Total (7440-02-0)	X			<0.005	<0.433					1	mg/L	1b.	n/a	n/a	n/a
10M. Selenium, Total (7782-49-2)	X			<0.005	<0.433					1	mg/L	1b.	n/a	n/a	n/a
11M. Silver, Total (7440-22-4)	X			<0.002	<0.177					1	mg/L	1b.	n/a	n/a	n/a
12M. Thallium, Total (7440-28-0)	X			<0.005	<0.433					1	mg/L	1b.	n/a	n/a	n/a
13M. Zinc, Total (7440-66-6)	X			0.008	0.709					1	mg/L	1b.	n/a	n/a	n/a
14M. Cyanide, Total (57-12-5)	X			<0.005	<0.433					1	mg/L	1b.	n/a	n/a	n/a
15M. Phenols, Total	X			0.0433	3.84					1	mg/L	1b.	n/a	n/a	n/a
DIOXIN															
2,3,7,8-Tetra-chlorodibenzo-P-Dioxin (1784-01-6)			X	DESCRIBE RESULTS Not applicable											

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CONTINUE ON REVERSE

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1 POLLUTANT AND CAS NUMBER (if available)	2 MARK "X"			3. EFFLUENT								4 UNITS			5. INTAKE (optional)		
	a TESTING REQUIRED	b BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES		
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS			
GC/MS FRACTION - VOLATILE COMPOUNDS																	
1V. Acrolein (107-02-8)	X			<0.0500	<4.433					1	mg/L	1b.	n/a	n/a	n/a		
2V. Acrylonitrile (107-13-1)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
3V. Benzene (71-43-2)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
4V. Bis (Chloromethyl) Ether (542-88-1)			X	Not Reg	ired	per NCDWR	NPDES	Permitt'g	Unit								
5V. Bromoform (75-25-2)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
6V. Carbon Tetrachloride (56-23-5)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
7V. Chlorobenzene (108-90-7)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
8V. Chlorobromomethane (124-48-1)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
9V. Chloroethane (75-00-3)	X			<0.00500	<0.443					1	mg/L	1b.	n/a	n/a	n/a		
10V. 2-Chloroethylvinyl Ether (110-75-8)	X			<0.0500	<4.433					1	mg/L	1b.	n/a	n/a	n/a		
11V. Chloroform (67-66-3)	X			0.0248	2.199					1	mg/L	1b.	n/a	n/a	n/a		
12V. Dichlorobromomethane (75-27-4)	X			0.00422	0.374					1	mg/L	1b.	n/a	n/a	n/a		
13V. Dichlorodifluoromethane (75-71-8)	X			<0.00500	<0.443					1	mg/L	1b.	n/a	n/a	n/a		
14V. 1,1-Dichloroethane (75-34-3)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
15V. 1,2-Dichloroethane (107-06-2)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
16V. 1,1-Dichloroethylene (75-35-4)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
17V. 1,2-Dichloropropane (78-67-5)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
18V. 1,3-Dichloropropylene (542-75-8)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
19V. Ethylbenzene (100-41-4)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
20V. Methyl Bromide (74-83-8)	X			<0.00500	<0.443					1	mg/L	1b.	n/a	n/a	n/a		
21V. Methyl Chloride (74-87-3)	X			<0.00250	<0.222					1	mg/L	1b.	n/a	n/a	n/a		

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1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS			5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	e. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES		
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS			
GC/MS FRACTION - VOLATILE COMPOUNDS (continued)																	
22V. Methylene Chloride (75-09-2)	X			<0.00500	<0.443					1	mg/L	1b.	n/a	n/a	n/a		
23V. 1,1,2,2-Tetrachloroethane (79-34-6)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
24V. Tetrachloroethylene (127-18-4)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
25V. Toluene (108-88-3)	X			<0.00500	<0.443					1	mg/L	1b.	n/a	n/a	n/a		
26V. 1,2-Trichloroethylene (156-60-5)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
27V. 1,1,1-Trichloroethane (71-55-6)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
28V. 1,1,2-Trichloroethane (79-00-5)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
29V. Trichloroethylene (79-01-6)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
30V. Trichlorofluoromethane (75-68-4)	X			<0.00500	<0.443					1	mg/L	1b.	n/a	n/a	n/a		
31V. Vinyl Chloride (75-01-4)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a		
GC/MS FRACTION - ACID COMPOUNDS																	
1A. 2-Chlorophenol (85-57-8)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
2A. 2,4-Dichlorophenol (120-83-2)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
3A. 2,4-Dimethylphenol (105-67-9)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
4A. 4,6-Dinitro-O-Cresol (534-52-1)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
5A. 2,4-Dinitrophenol (51-28-5)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
6A. 2-Nitrophenol (88-75-5)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
7A. 4-Nitrophenol (100-02-7)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
8A. p-Chloro-M-Cresol (59-50-7)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
9A. Pentachlorophenol (87-86-5)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
10A. Phenol (106-95-2)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		
11A. 2,4,6-Trichlorophenol (88-05-2)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a		

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CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT						4. UNITS		5. INTAKE (optional)			
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS															
18. Acenaphthene (83-32-9)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
28. Acenaphthylene (206-86-8)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
36. Anthracene (120-12-7)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
48. Benzidine (92-87-5)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a
58. Benzo (a) Anthracene (56-55-3)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
68. Benzo (a) Pyrene (50-32-8)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
78. 3,4-Benzofluoranthene (205-99-2)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
88. Benzo (ghi) Perylene (191-24-2)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
98. Benzo (h) Fluoranthene (207-08-9)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
108. Bis (2-Chloro-4-methyl) Methane (111-91-1)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a
118. Bis (2-Chloro-4-methyl) Ether (111-44-4)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a
128. Bis (2-Chloro-4-methyl) Ether (102-90-1)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a
138. Bis (2-Dichloro-4-methyl) Phthalate (117-81-7)	X			<0.00300	<0.266					1	mg/L	1b.	n/a	n/a	n/a
148. 4-Bromophenyl Phenyl Ether (101-55-3)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a
158. Butyl Benzyl Phthalate (85-68-7)	X			<0.00300	<0.266					1	mg/L	1b.	n/a	n/a	n/a
168. 2-Chloronaphthalene (91-58-7)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
178. 4-Chlorophenyl Phenyl Ether (7005-72-3)	X			<0.0100	<0.887					1	mg/L	1b.	n/a	n/a	n/a
188. Chrysene (218-01-9)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
198. Dibenzo (a,h) Anthracene (53-70-3)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
208. 1,2-Dichlorobenzene (95-50-1)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
218. 1,3-Dichlorobenzene (541-73-1)	X			<0.00100	<0.089					1	mg/L	1b.	n/a	n/a	n/a
										1	mg/L	1b.	n/a	n/a	n/a

EPA Form 3510-2C (8-90)

PAGE 5

EPA Form 3510-2C (8-90)

PAGE V-6

CONTINUE ON PAGE V-7

OUTFALL 002

CONTINUED FROM PAGE V-6

CONTINUED FROM PAGE 1-6

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS		5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS		
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS (continued)																
228. 1,4-Dichlorobenzene (106-46-7)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a	
238. 3,3-Dichlorobenzidine (91-94-1)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
248 Diethyl Phthalate (84-66-2)	X			<0.00300	<0.226					1	mg/L	lb.	n/a	n/a	n/a	
258. Dimethyl Phthalate (131-11-3)	X			<0.00300	<0.226					1	mg/L	lb.	n/a	n/a	n/a	
268. Di-N-Butyl Phthalate (84-74-2)	X			<0.00300	<0.226					1	mg/L	lb.	n/a	n/a	n/a	
278. 2,4-Dinitrotoluene (121-14-2)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
288. 2,6-Dinitrotoluene (806-20-2)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
298. Di-N-Octyl Phthalate (117-84-0)	X			<0.00300	<0.226					1	mg/L	lb.	n/a	n/a	n/a	
308 1,2-Diphenylhydrazine (as Azobenzene) (122-66-7)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
318. Fluoranthene (206-44-0)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a	
328. Fluorene (86-73-7)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a	
338. Hexachlorobenzene (118-74-1)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a	
348. Hexachlorobutadiene (87-66-3)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
358. Hexachlorocyclopentadiene (77-47-4)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
368 Hexachloroethane (87-72-1)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
378. Indeno (1,2,3-cd) Pyrene (183-39-5)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a	
388. Isophorone (78-59-1)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
398. Naphthalene (91-20-3)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a	
408. Nitrobenzene (98-95-3)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
418 N-Nitrosodimethylamine (62-75-9)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	
428. N-Nitrosodi-N-Propylamine (621-64-7)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a	

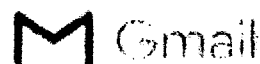
OUTFALL 002

CONTINUED FROM THE FRONT

CONTINUED FROM THE FRONT															
1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT						4. UNITS			5. INTAKE (optional)		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO OF ANALYSES
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
GC/MS FRACTION - BASE/NEUTRAL COMPOUNDS (continued)															
43B. N-Nitrosodiphenylamine (86-30-6)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a
44B. Phenanthrene (85-01-6)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a
45B. Pyrene (129-00-0)	X			<0.00100	<0.089					1	mg/L	lb.	n/a	n/a	n/a
46B. 1,2,4-Trichlorobenzene (120-82-1)	X			<0.0100	<0.887					1	mg/L	lb.	n/a	n/a	n/a
GC/MS FRACTION - PESTICIDES															
1P. Aldrin (309-00-2)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
2P. α-BHC (319-84-6)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
3P. β-BHC (319-85-7)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
4P. γ-BHC (59-88-9)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
5P. δ-BHC (319-86-8)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
6P. Chlordane (57-74-9)	X			<0.000050	<0.044					1	mg/L	lb.	n/a	n/a	n/a
7P. 4,4'-DDT (50-29-3)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
8P. 4,4'-DDE (72-35-9)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
9P. 4,4'-DDD (72-54-8)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
10P. Dieldrin (60-57-1)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
11P. α-Endosulfan (115-29-7)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
12P. β-Endosulfan (115-29-7)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
13P. Endosulfan Sulfate (1031-07-8)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
14P. Endrin (72-20-8)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
15P. Endrin Aldehyde (7421-93-4)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
16P. Heptachlor (76-44-8)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a

OUTFALL 002

CONTINUED FROM PAGE V-8			EPA I.D. NUMBER (copy from Item 1 of Form I)		OUTFALL NUMBER										
			NCD 047 368 642		002										
1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT						4. UNITS		5. INTAKE (optional)			
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	a. LONG TERM AVERAGE VALUE		b. NO. OF ANALYSES
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				(1) CONCENTRATION	(2) MASS	
GC/MS FRACTION - PESTICIDES (continued)															
17P. Heptachlor Epoxide (1024-57-3)	X			<0.000050	<0.005					1	mg/L	lb.	n/a	n/a	n/a
18P. PCB-1242 (53488-21-6)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
19P. PCB-1254 (11067-68-1)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
20P. PCB-1221 (11104-28-2)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
21P. PCB-1232 (11141-16-5)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
22P. PCB-1248 (12672-29-6)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
23P. PCB-1260 (11066-82-6)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
24P. PCB-1016 (12674-11-2)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a
25P. Toxaphene (8001-35-2)	X			<0.000500	<0.044					1	mg/L	lb.	n/a	n/a	n/a



Linda Miles <milesfirm@gmail.com>

FW: POTENTIAL statement from Brunswick Co

2 messages

Linda Miles <Linda.Miles@cfpua.org>
To: Linda Miles Firm <milesfirm@gmail.com>

Thu, Jun 8, 2017 at 1:27 PM

From: Frank Styers
Sent: Thursday, June 8, 2017 1:26:59 PM (UTC-05:00) Eastern Time (US & Canada)
To: Jim Flechtner; Beth Eckert; Carel Vandermeiden; Linda Miles
Subject: FW: POTENTIAL statement from Brunswick Co

FYI

From: Amanda Hutcheson [mailto:amanda.hutcheson@brunswickcountync.gov]
Sent: Thursday, June 08, 2017 1:00 PM
To: Frank Styers <Frank.Styers@cfpua.org>
Subject: POTENTIAL statement from Brunswick Co

Mr. Styers,

Good afternoon. Thank you for taking the time on the phone this morning to share information and discuss our efforts.

Attached and below, I am including a potential statement that we are considering sending out. It has not been released; we just wanted to send a copy for you to see, in case it is.

If you have any questions or concerns, please let me know,

Amanda Hutcheson
Public Information Officer
Brunswick County
30 Government Center Drive, NE
PO Box 249
Bolivia, NC 28422

910-253-2995

Facebook Twitter Google +

Brunswick County Media Release



For immediate release: 6/8/17

Contact: Amanda Hutcheson, (910) 253-2995

Amanda.hutcheson@brunswickcountync.gov

Statement on GenX, Water Quality Standards

Bolivia, NC – A recent media report has touched on the presence of the chemical GenX in the Cape Fear River, from which Brunswick County Public Utilities (BCPU), Cape Fear Public Utility Authority and Pender County Utilities draw portions of their raw water supply. This chemical is made by a company named Chemours, located on the Cape Fear River upstream from Wilmington, where it is suspected the chemical's presence in the river originates.

Water from BCPU meets all EPA and state standards regarding water quality, including monitoring for the presence and concentration of dozens of different chemicals and substances, with the results of more than 25 of those substances reported annually. The EPA has a process to evaluate new chemicals to determine their potential impact at different levels and to set quality and safety standards, if any are needed; currently, GenX and approximately 700 other chemicals are in this process and being monitored. At this time, data is not readily available on whether or not this is a chemical of concern, nor are commercial labs currently testing for the presence or concentration of this specific chemical. The EPA is in a better position, with greater resources, than Brunswick County to make these evaluations and set these standards and guidelines.

Brunswick County Public Utilities and other public utility providers are sharing information about this new chemical. Local utilities have requested additional information from the NC Department of Environmental Quality, and BCPU looks forward to receiving any additional information provided. BCPU will follow any additional information or guidance resulting from this inquiry or the EPA process.

Brunswick County Public Utilities takes seriously its commitment to providing safe, quality drinking water to its citizens and customers.

– End –

2 attachments



image001.png
21K

060817 Water Quality Testing and Standards.docx
40K

Linda Miles <milesfirm@gmail.com>
To: GHOUSE <GHOUSE@brookspierce.com>

Thu, Jun 8, 2017 at 5:33 PM

Brunswick County

----- Forwarded message -----

From: **Linda Miles** <Linda.Miles@cfpua.org>

Date: Thu, Jun 8, 2017 at 1:27 PM

Subject: FW: POTENTIAL statement from Brunswick Co

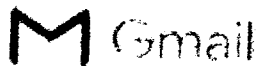
[Quoted text hidden]

2 attachments



image001.png
21K

 **060817 Water Quality Testing and Standards.docx**
40K



Linda Miles <milesfirm@gmail.com>

Fwd: Wilmington Star News

1 message

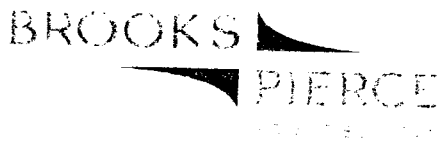
George House <GHOUSE@brookspierce.com>

Sun, Jun 11, 2017 at 11:20 PM

To: Linda Miles <milesfirm@gmail.com>

Our librarian got all of news articles for me. I think the biggest question is how can Chemours discharge it if EPA approved its use on condition it would not be discharged.

George House



correspondence

t: 336.271.3114

f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

Begin forwarded message:

From: "Jayant Joshi" <JJOSHI@brookspierce.com>
To: "George House" <GHOUSE@brookspierce.com>
Cc: "Jennifer Griffin Scotton" <jscotton@brookspierce.com>, "Walker Douglas" <WDOUGLAS@brookspierce.com>
Subject: RE: Wilmington Star News

I don't have this login either. However, for some reason I was able to get to all their content without signing in so I've attached the most recent articles involving the CFPUA.

I'll call the paper first thing in the morning. We have a print subscription, so I should be able to get this fixed.

Thanks.

Jayant Joshi, Librarian & Research Specialist

t: 336.232.4646
f: 336.232.9146

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

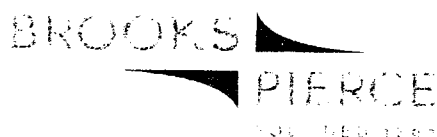
From: Jennifer Griffin Scotton
Sent: Sunday, June 11, 2017 3:14 PM
To: Walker Douglas <WDOUGLAS@brookspierce.com>
Cc: George House <GHOUSE@brookspierce.com>; IT Help Desk <helpdesk@brookspierce.com>; Teresa C. Plunkett <TPlunkett@BrooksPierce.com>; Jayant Joshi <JJOSHI@brookspierce.com>
Subject: Re: Wilmington Star News

Unfortunately I do not have the login information. I'm adding Jayant to this chain in the event that he has the info as he maintains some of our publication logins.

Thank you,

Jennifer

Jennifer Griffin Scotton, Director of Marketing



t: 919.882.2500
f: 336.232.9088

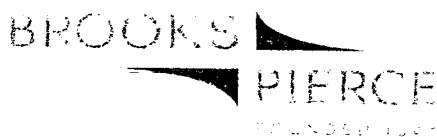
1700 Wells Fargo Capitol Center
150 Fayetteville Street
Raleigh, NC 27601
P.O. Box 1800 (27602)

On Jun 11, 2017, at 12:50 PM, Walker Douglas <WDOUGLAS@brookspierce.com> wrote:

I believe at one point we had a contract with the Wilmington Star News for search engine optimization or some other marketing purposes. I am copying Jennifer on this response in case we still have the contract with them. If so, she may know the login information. When I am in the office tomorrow I will look at the contract. I think I still have it in my files.

Walker

Walker Douglas, Director of Administration



t: 336.271.2565
f: 336.232.9165

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

On Jun 11, 2017, at 12:20 PM, George House <GHOUSE@brookspierce.com> wrote:

I am trying to read articles on the Wilmington Star for our client the Cape Fear Utility Authority, but when I try to sign in it says we already have an account. Do any of you know how we sign in to an account?

George House

<image001.jpg>

t: 336.271.3114
f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)


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e-mail to the intended recipient, any disclosure of this information in any way or taking of any action in reliance on this information is strictly prohibited. If you have received this e-mail in error, please notify the person transmitting the information immediately.

This e-mail message has been scanned and cleared by MailMarshal SMTP.

24 attachments

 **Previous contamination led to EPA fine, \$671 million settlement - News - Wilmington Star News - Wilmington, NC.pdf**
109K

 **ATT00001.htm**
1K

 **Toxin taints CFPUA drinking water - News - Wilmington Star News - Wilmington, NC.pdf**
311K

 **ATT00002.htm**
1K

 **Local officials respond to presence of GenX in Cape Fear water.pdf**
109K

 **ATT00003.htm**
1K

 **Study_ Pre-GenX chemicals are likely still in your water.pdf**
118K

 **ATT00004.htm**
1K

 **NC pushes Chemours for GenX information, action.pdf**
112K


 **ATT00005.htm**
1K

 **FROM THE EDITOR_ We will stick with toxic water investigation - News - Wilmington Star News - Wilmington, NC.pdf**
111K

 **ATT00006.htm**
1K

 **New Hanover, Wilmington officials to meet with Chemours over GenX - News - Wilmington Star News - Wilmington, NC.pdf**
114K

 **ATT00007.htm**
1K

 **OPINION_ CFPUA's top priority safe, clean water - Opinion - Wilmington Star News - Wilmington, NC.pdf**
101K

 **ATT00008.htm**
1K

 **EDITORIAL, June 11_ Chemours, stop tainting our water – now.pdf**
241K




ATT00009.htm

1K

 **GenX fallout_ Is my water safe to drink_.pdf**
108K

 **ATT00010.htm**
1K

 **TOXIC FAQs_ What we know and what we don't know - News - Wilmington Star News -
Wilmington, NC.pdf**
115K

 **ATT00011.htm**
1K

 **Toxin taints CFPWA drinking water.pdf**
319K

 **ATT00012.htm**
1K



Linda Miles <milesfirm@gmail.com>

Lab1 message

Beth Eckert <Beth.Eckert@cfpua.org>

Thu, Jun 15, 2017 at 3:26 AM

To: Jim Flechtner <jim.flechtner@cfpua.org>, Frank Styers <Frank.Styers@cfpua.org>, Linda Miles <milesfirm@gmail.com>, Lindsey Hallock <Lindsey.Hallock@cfpua.org>, Eric Hatcher <eric.hatcher@cfpua.org>, Carel Vandermeiden <Carel.Vandermeiden@cfpua.org>

Cc: Jill Deaney <Jill.Deaney@cfpua.org>

Hey guys

Our contract lab, Eurofins, contacted jill yesterday and they have been looking into how they can test for this compound.. They said think they have identified where they can get a standard and if we would like to send them samples they will get it ordered. They could have it in about a week. They stated they would have to analyze doing a method similar to 537 but not exactly. I bring this up because they may can get results quicker than the time frames quoted by the Colorado lab Deq and Chemours mentioned. This is our contract lab we deal with on all of our other organic type testing and we have a relationship with them already. Do we want to explore further this additional testing path?

Thanks,

Beth Eckert



Linda Miles <milesfirm@gmail.com>

Confidential: Attorney client

2 messages

Beth Eckert <Beth.Eckert@cfpua.org>

Thu, Jun 15, 2017 at 5:13 AM

To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>, Jim Flechtner <jim.flechtner@cfpua.org>, Frank Styers <Frank.Styers@cfpua.org>, Lindsey Hallock <Lindsey.Hallock@cfpua.org>

George,

Maybe I'm missing something but based on the conference call yesterday I'm confused. The toxicologist from the EPA health and human services area stated - the 70,000 ppt long term exposure value was developed based on the most vulnerable population which includes infants, elderly, and those with compromised immune systems and that this value is considered by them to be protective of public health even for these populations. I know they did not come right out and say our water is safe and I don't think they ever will. There are too many other potential issues outside of genx for them to make that direct of a statement. Did I misunderstand something on the call?

For the sake of our community and to restore public confidence, the compliance of Chemours with the consent order and their permit are definitely items we need to explore further with DEQ and EPA to ensure it is being properly regulated and the ongoing oversight is there with the establishment of some standards and testing requirements within their permit. However, the concentration above is substantially higher than what we found in the water and they said the value is protective of public health.....

Please let me know what I'm missing as I'm not trying to downplay the issue as I remain very concerned but their statements yesterday gave me some reassurance of the safety of the water and potential language we can use to begin rebuilding that consumer confidence along with some ongoing analysis.

Please let me know your thoughts and if I'm misunderstanding.

Thanks,
Beth Eckert

George House <GHOUSE@brookspierce.com>

Thu, Jun 15, 2017 at 7:21 AM

To: Beth Eckert <Beth.Eckert@cfpua.org>, Linda Miles <milesfirm@gmail.com>, Jim Flechtner <jim.flechtner@cfpua.org>, Frank Styers <Frank.Styers@cfpua.org>, Lindsey Hallock <Lindsey.Hallock@cfpua.org>

See my responses below.

In the back of my mind, I have a nagging concern that this "standard" is based upon only one study - which I am not sure it has been replicated and which GenX compound(s) it covered are not clear. When I tried to get EPA to agree to the same, the EPA representatives said they needed to defer to HQs.

George House

Brooks Pierce

t: 336.271.3114
f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401

P.O. Box 26000 (27420)

-----Original Message-----

From: Beth Eckert [mailto:Beth.Eckert@cfpua.org]

Sent: Thursday, June 15, 2017 5:13 AM

To: Linda Miles <milesfirm@gmail.com>; George House <GHOUSE@brookspierce.com>; Jim Flechtner <jim.flechtner@cfpua.org>; Frank Styers <Frank.Styers@cfpua.org>; Lindsey Hallock <Lindsey.Hallock@cfpua.org>

Subject: Confidential: Attorney client

George,

Maybe I'm missing something but based on the conference call yesterday I'm confused. The toxicologist from the EPA health and human services area stated - the 70,000 ppt long term exposure value was developed based on the most vulnerable population which includes infants, elderly, and those with compromised immune systems and that this value is considered by them to be protective of public health even for these populations. I know they did not come right out and say our water is safe and I don't think they ever will. There are too many other potential issues outside of genx for them to make that direct of a statement. Did I misunderstand something on the call?

This is what I heard the representative of DHHS say and she then repeated it based upon the "European Study". I think that is the one you already sent to me.

For the sake of our community and to restore public confidence, the compliance of Chemours with the consent order and their permit are definitely items we need to explore further with DEQ and EPA to ensure it is being properly regulated and the ongoing oversight is there with the establishment of some standards and testing requirements within their permit. However, the concentration above is substantially higher than what we found in the water and they said the value is protective of public health.....

Yes. Remember, the same spokesperson started her comments by saying the standard they believe is protective was "100 times higher" than our highest sample.

Please let me know what I'm missing as I'm not trying to downplay the issue as I remain very concerned but their statements yesterday gave me some reassurance of the safety of the water and potential language we can use to begin rebuilding that consumer confidence along with some ongoing analysis.

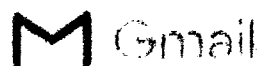
Please let me know your thoughts and if I'm misunderstanding.

Thanks,
Beth Eckert

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This e-mail message has been scanned and cleared by M86 MailMarshal.



Linda Miles <milesfirm@gmail.com>

attorney-client privilege/ private & confidential

1 message

Donna Pope <Donna.Pope@cfpua.org>

Tue, Jun 13, 2017 at 1:07 PM

To: "George House <GHOUSE@brookspierce.com> (GHOUSE@brookspierce.com)"

<GHOUSE@brookspierce.com>, Linda Miles <milesfirm@gmail.com>

George, here are notes from a conversation Linda had today with Gary Shipman, who called us with information he wanted to share.



Shipman memorandum 6.13.2017.pdf

207K

NOTICE: E-Mail correspondence to and from this address may be subject to the NC Public Records Law and may be disclosed to third parties.

From: Frank Styers
Sent: Tuesday, June 13, 2017 10:24 AM
To: John Malone <John.Malone@cfpu.org>
Subject: Fwd: GREENSBORO-#1089268-v1-Cape_Fear_GenX_Resolution

Can you provide river stream distance?

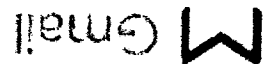
Sent from my iPhone

Begin forwarded message:

From: Donna Pope <Donna.Pope@cfpu.org>
Date: June 13, 2017 at 10:11:52 AM EDT
To: Frank Styers <Frank.Styers@cfpu.org>
Cc: Linda Miles <milesfirm@gmail.com>, Jim Flechtner <jim.flechtner@cfpu.org>
Subject: FW: GREENSBORO-#1089268-v1-Cape_Fear_GenX_Resolution

[Quoted text hidden]

 Chemours Company to Kings Bluff - Overview.pdf 701K



Linda Miles <milesfirm@gmail.com>

Contract Terms

13 messages

Mon, Jun 12, 2017 at 5:51 PM

Pres Davenport <pres@eandvgroup.com>
To: Milesfirm@gmail.com
Cc: Mike Brown <mike@capetearecommercial.com>

Miles -

Mike Brown asked me to connect with you. We are in the process of contracting with the CFPUA to help strategically manage media and messaging surrounding the GenX issue.

It is our understanding that the CFPUA has standard terms that they would like to use. Would you mind please sending those to me so that I can have our legal review them and incorporate our draft scope of work for review.

Thank you -

Pres

Pres Davenport
Partner / Business Development Director
Eckel & Vaughan

WRK 919-619-0764
EML pres@eandvgroup.com
WEB www.EandVgroup.com

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milesfirm@gmail.com <milesfirm@gmail.com>
To: Pres Davenport <pres@eandvgroup.com>
Mon, Jun 12, 2017 at 5:59 PM

Will get Julia Vosnock to send

Sent from my iPhone

[Quoted text hidden]

milesfirm@gmail.com <milesfirm@gmail.com>
To: Julia Vosnock <julia.vosnock@cfpu.org>
Mon, Jun 12, 2017 at 6:01 PM

Can you send these folks. Our standard consultant contracts for pop

Sent from my iPhone

Begin forwarded message:

From: Pres Davenport <pres@eandvgroup.com>
Date: June 12, 2017 at 5:51:15 PM EDT
To: Milesfirm@gmail.com
Cc: Mike Brown <mike@capdefearcommercial.com>
Subject: Contract Terms

[Quoted text hidden]

Pres Davenport <pres@eandvgroup.com>
To: milesfirm@gmail.com
Mon, Jun 12, 2017 at 6:11 PM

Thank you

Pres Davenport
Partner / Business Development Director
Eckel & Vaughan

WRK 919-619-0764
EML pres@eandvgroup.com
WEB www.EandVgroup.com

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[Quoted text hidden]

Pres Davenport <pres@eandvgroup.com>
To: milesfirm@gmail.com
Tue, Jun 13, 2017 at 7:04 AM

Linda, my apologies. I was never given your name. Sorry for calling you the wrong thing.

Thanks for your help.

Pres

Pres Davenport
Partner / Business Development Director
Eckel & Vaughan

WRK 919-619-0764
EML pres@eandvgroup.com
WEB www.EandVgroup.com

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[Quoted text hidden]

Julia Vosnock <julia.vosnock@cfpua.org>
To: "pres@eandvgroup.com" <pres@eandvgroup.com>
Cc: Linda Miles <milesfirm@gmail.com>

Pres,

Linda Miles asked that I send you our standard consultant contract. I have attached. Let me know if you have any questions.

Thanks,

Julia Vosnock, MBA, CLGPO

Procurement Manager

Cape Fear Public Utility Authority

235 Government Center Drive

Suite 201 (2nd Floor)


Wilmington, NC 28403

Phone: 910-332-6589

Fax: 910-799-6066

From: milesfirm@gmail.com [mailto:milesfirm@gmail.com]
Sent: Monday, June 12, 2017 6:02 PM
To: Julia Vosnock <julia.vosnock@cfpua.org>
Subject: Fwd: Contract Terms

[Quoted text hidden]

 Professional Services Contract Template.docx 39K

Pres Davenport <pres@eandvgroup.com>

Wed, Jun 14, 2017 at 9:01 AM

To: Julia Vosnock <julia.vosnock@cfpa.org>
Cc: Linda Miles <milesfirm@gmail.com>

Thank you Julia. I am working of the Scope of Services Attachment A. What is typically included in the "purpose" section and how is that different from the scope of services language?

Pres Davenport
Partner / Business Development Director
Eckel & Vaughan

WRK 919-619-0764
EML pres@eandvgroup.com
WEB www.EandVgroup.com

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[Quoted text hidden]

[Quoted text hidden]

<Professional Services Contract Template.docx>

Julia Vosnock <julia.vosnock@cfpa.org>
To: Pres Davenport <pres@eandvgroup.com>
Cc: Linda Miles <milesfirm@gmail.com>

Purpose is just a very brief description, usually one sentence about the services to be provided. For this contract it could be "Cape Fear Public Utility Authority is contracting with the CONSULTANT to help strategically manage media and messaging."

The scope is more detailed about actual services to be provided.

Hope this helps,

Julia Vosnock, MBA, CLGPO

Procurement Manager

Cape Fear Public Utility Authority

235 Government Center Drive

Suite 201 (2nd Floor)

Wilmington, NC 28403
Phone: 910-332-6589
Fax: 910-799-6066

From: Pres Davenport [mailto:pres@eandvgroup.com]
Sent: Wednesday, June 14, 2017 9:01 AM
To: Julia Vosnock <julia.vosnock@cfpa.org>
Cc: Linda Miles <milesfirm@gmail.com>
Subject: Re: Contract Terms

[Quoted text hidden]

Julia Vosnock <julia.vosnock@cfpa.org>
To: Pres Davenport <pres@eandvgroup.com>
Cc: Linda Miles <milesfirm@gmail.com>

Also if you want to just send me your scope I can put the contract together.

Thanks,

Julia Vosnock, MBA, CLGPO
Procurement Manager
Cape Fear Public Utility Authority
235 Government Center Drive
Suite 201 (2nd Floor)
Wilmington, NC 28403

Phone: 910-332-6589
Fax: 910-799-6066

From: Pres Davenport [mailto:pres@eandvgroup.com]
Sent: Wednesday, June 14, 2017 9:01 AM
To: Julia Vosnock <julia.vosnock@cfpa.org>
Cc: Linda Miles <milesfirm@gmail.com>
Subject: Re: Contract Terms

Thank you Julia. I am working of the Scope of Services Attachment A. What is typically included in the "purpose" section and how is that different from the scope of services language?

[Quoted text hidden]

Pres Davenport <pres@eandvgroup.com>
To: Julia Vosnock <julia.vosnock@cfpa.org>
Cc: Linda Miles <milesfirm@gmail.com>, Mike Brown <mike@capitearcommercial.com>

Julia -

Attached is a basic scope of work. Please let me know if you have any questions, or if there is anything more I can do to be helpful. Our attorney is currently reviewing the contract terms to make sure we don't have any questions there. I have been told that he will get back to me by 3 today.

Thank you -

Pres

Pres Davenport
Partner / Business Development Director
Eckel & Vaughan

WRK 919-619-0764
EML pres@eandvgroup.com
WEB www.EandVgroup.com

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[Quoted text hidden]

 **E&V Estimate for CFPUA.docx** 550K

Julia Vosnock <julia.vosnock@cfpa.org>
To: Linda Miles <milesfirm@gmail.com>
Wed, Jun 14, 2017 at 1:37 PM

Linda,

Can we discuss?

Thanks,

Fax: 910-799-6066

<https://mail.google.com/mail/u/0/?ui=2&ik=79b349a7c3&view=pic&q=chemours&qqs=true...> 6/15/2017

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On Jun 14, 2017, at 4:43 PM, Pres Davenport <Pres@eandvgroup.com> wrote:

Julia -

I haven't heard back from you since sending the scope, so I have attempted to put together a completed agreement. This document has a proposed attachment a and attachment b. At our attorney's suggestion, we added language to Clause D - non waiver of rights to make them mutual. If this will work for you all please let me know and we will sign and send over a completed agreement immediately. If you need to make any other changes, please make them, let me know what they are, and we will do our best to review/approve and sign as soon as possible.

Thank you-

Pres

Pres Davenport
Partner / Business Development Director
Eckel & Vaughan

WRK 919-619-0764

EML Pres@eandvgroup.com
WEB www.EandVgroup.com

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<E&V Estimate for CFPUA.docx>

[Quoted text hidden]

[Quoted text hidden]

 Professional Services Contract Eckel & Vaughan CFPUA 6.15.17 Draft.docx 45K

Thu, Jun 15, 2017 at 9:08 AM

Julia Vosnock <julia.vosnock@cfpu.org>

To: Pres Davenport <pres@eandvgroup.com>

Cc: Linda Miles <milesfirm@gmail.com>, Mike Brown <mike@capitearcommercial.com>, Jim Flechtner <jim.flechtner@cfpu.org>, Albert Eckel <albert@eandvgroup.com>

Pres,

Thank you. I will need three signed copies of the agreement and your insurance certificates. If you are going to be here today or tomorrow, I can arrange for a notary at our office and you can sign them here if that is easier for you. I did change the signature page to reflect an LLC. Also I have attached our vendor forms, which I will need to set you up as a vendor in our system. Please let me know if you have any questions.

Thanks,

Julia Vosnock, MBA, CLGPO

Procurement Manager

Cape Fear Public Utility Authority

235 Government Center Drive

Suite 201 (2nd Floor)

Wilmington, NC 28403

Phone: 910-332-6589

Fax: 910-799-6066

From: Pres Davenport [mailto:pres@eandvgroup.com]
Sent: Thursday, June 15, 2017 8:42 AM
To: Julia Vosnock <julia.vosnock@cfpa.org>
Cc: Linda Miles <milesfirm@gmail.com>; Mike Brown <mike@capfeearcommercial.com>; Jim Flechtner <jim.flechtner@cfpa.org>; Albert Eckel <albert@eandvgroup.com>
Subject: Re: Contract Terms

[Quoted text hidden]

2 attachments

 New Vendor Cover Letter and Forms.pdf 3161K

 Professional Services Contract Eckel Vaughan CFPUA 6.15.17 Final.pdf 1044K



Linda Miles <milesfirm@gmail.com>

Lab

1 message

Beth Eckert <Beth.Eckert@cfpua.org> Thu, Jun 15, 2017 at 3:26 AM

To: Jim Flechtner <jim.flechtner@cfpua.org>, Frank Styers <Frank.Styers@cfpua.org>, Linda Miles <milesfirm@gmail.com>, Lindsey Hallock <Lindsey.Hallock@cfpua.org>, Eric Hatcher <eric.hatcher@cfpua.org>, Carel Vandermeijden <Carel.Vandermeijden@cfpua.org>
Cc: Jill Deane <jill.Deaney@cfpua.org>

Hey guys

Our contract lab, Eurofins, contacted Jill yesterday and they have been looking into how they can test for this compound. They said think they have identified where they can get a standard and if we would like to send them samples they will get it ordered. They could have it in about a week. They stated they would have to analyze doing a method similar to 537 but not exactly. I bring this up because they may can get results quicker than the time frames quoted by the Colorado lab. Deg and Chemours mentioned. This is our contract lab we deal with on all of our other organic type testing and we have a relationship with them already. Do we want to explore further this additional testing path?

Thanks,
Beth Eckert

From: Dettel Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, June 13, 2017 11:50 PM
To: Frank Styers <Frank.Styers@cfpu.org>
Cc: John Malone <John.Malone@cfpu.org>; Beth Eckert <Beth.Eckert@cfpu.org>; Ben Keams <Ben.Keams@cfpu.org>
Subject: Re: Voice mail

Hi Frank,

See my answers in CAPS below. Please let me know if clarifications are needed.

Thank you,

Dettel

On 6/13/17 2:04 PM, Frank Styers wrote:

Dettel,

I was wondering if you could answer the questions below:

- Did you originally expect that you would detect GenX in the samples and if so why?

MY EPA COLLABORATORS ANDREW LINDSTROM AND MARK STRYNAR BEGAN IN 2012 TO SEARCH FOR THE IDENTITY OF THE COMPOUND THAT DUPONT INTRODUCED AS A REPLACEMENT FOR PFOA. THEIR WORK LED TO THE IDENTIFICATION OF GENX AND LATER THE OTHER ETHERS IN THE CAPE FEAR RIVER DOWNSTREAM OF THE CHEMOURS PLANT. THEIR WORK WAS PUBLISHED IN THE ATTACHED 2015 ARTICLE THAT APPEARED IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY. MY STUDENTS BEGAN TO MEASURE GENX CONCENTRATIONS IN 2013, WHEN THE COMPANY WELLINGTON LABS INTRODUCED AN ANALYTICAL STANDARD FOR GENX (THEY CALL IT HFPO DIMER ACID - SEE http://www.well-labs.com/docs/hfpoda_m3hfpoda_20feb2013_wellington_reporter.pdf).

- The agreement for the GenX study was signed in the fall of 2015 but your samples were from 2013 and -14. Could you please explain the origin of the data, when were the samples were taken and when they were analyzed for GenX?

WE COLLECTED 34 SAMPLES BETWEEN JUNE 14, 2013 AND DECEMBER 2, 2013. THESE SAMPLES WERE COMPOSITED DAILY SAMPLES COLLECTED AT THE RAW WATER TAP OF THE SWEENEY PLANT. ON AUGUST 18, 2014, WE COLLECTED GRAB SAMPLES FROM THE RAW AND FINISHED WATER TAPS AS WELL AS AT SAMPLING POINTS WITHING THE SWEENEY WTP TO ASSESS THE PERFORMANCE OF INDIVIDUAL UNIT PROCESSES FOR PFAS CONTROL. ALL SAMPLES WERE ANALYZED WITHIN 7

DAYS OF RECEIPT OF THE SAMPLES AT NC STATE UNIVERSITY.

- Was there any testing performed to confirm the existence after 2014?

EPA COLLABORATORS COLLECTED SAMPLES AGAIN ON DECEMBER 16, 2016. A CAPE FEAR RIVER SAMPLE COLLECTED NEAR TAR HEEL EXHIBITED A GENX CONCENTRATION OF 172 NG/L.

- Was this run on 537, how did you identify GenX within this method and where did you get the GenX standard? If not what method was used?

WE USED AN IN-HOUSE LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY METHOD TO DETERMINE THE CONCENTRATIONS OF GENX. THE ANALYTICAL METHOD IS DESCRIBED IN THE ATTACHED SUPPORTING INFORMATION OF THE 2016 PAPER BY SUN. THE INFORMATION DESCRIBES THE MASS SPECTROMETER SETTINGS FOR THE IDENTIFICATION OF GENX AND THE OTHER ETHERS. THE GENX STANDARD WAS OBTAINED FROM WELLINGTON LABS AS DESCRIBED UNDER POINT 1

- We understand that you worked with EPA (in Research Triangle Park) to develop the test method. Is this correct?

YES

- Did you (NCSU) perform all of the tests, or did you send the samples to a lab to be tested?

AN NCSU STUDENT AND POSTDOC MEASURED THE GENX CONCENTRATIONS USING INSTRUMENTATION AT THE EPA LAB IN RESEARCH TRIANGLE PARK. NO SAMPLES WERE SENT TO OUTSIDE LABS.

- In the study (Figure 2-Fate of Genx through the plant) it appears this data represents results from a single sampling event that occurred August 2014, or is this graph produced from a conglomeration of multiple samples?

FIGURE 2 REPRESENTS THE RESULTS OF A SINGLE SAMPLING EVENT. GRAB SAMPLES WERE COLLECTED ON AUGUST 18, 2014.

- Have other samples been taken from the river or processes?

WE COLLECTED SAMPLES ALONG THE CAPE FEAR RIVER AND AT THE SWEENEY WTP AT THE END OF MAY 2017. THESE RESULTS

ARE STILL PENDING.

• Can you further explain figure 2b?

FIGURE 2B ILLUSTRATES THAT IN ADDITION TO GENX (LABELED PFPORPA), HIGHLIGHTED IN THE DASHED OVAL, SIX ADDITIONAL PERFLUOROALKYL ETHER CARBOXYLIC ACIDS WERE DETECTED. NO ANALYTICAL STANDARDS WERE AVAILABLE FOR THE SIX ADDITIONAL COMPOUNDS. THEREFORE, WE CAN ONLY SHOW THE INSTRUMENT RESPONSE (PEAK AREA) FOR THESE COMPOUNDS. THREE COMPOUNDS (PFMOA, PFO2HXA, and PFO3OA) HAD PEAK AREAS THAT WERE 2-113 TIMES GREATER THAN THAT OF PFPORPA. PEAK AREA IS PROPORTIONAL TO CONCENTRATION. THESE RESULTS THEREFORE SUGGEST THAT THE CONCENTRATIONS OF PFMOA, PFO2HXA, and PFO3OA ARE SUBSTANTIALLY HIGHER THAN THE CONCENTRATION OF GENX. THE GENX CONCENTRATION IN THE FINISHED WATER WAS 474 NG/L ON AUGUST 18, 2014. ALSO, FIGURE 2B ILLUSTRATES THAT THE ADDITIONAL ETHER COMPOUNDS CANNOT BE REMOVED BY THE WATER TREATMENT PROCESSES EMPLOYED AT THE SWEENEY WTP.

Thanks,

Frank Styers

Office: (910) 332-6670

Cell (910) 515-5952

From: Dettel Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, June 13, 2017 12:27 AM
To: Ben Kearns <Ben.Kearns@ctfpa.org>
Cc: Frank Styers <Frank.Styers@ctfpa.org>; John Malone <John.Malone@ctfpa.org>
Subject: Re: Voice mail

Frank,

I will call you tomorrow at 11:45.

Dettel

On 6/12/17 6:30 PM, Ben Kearns wrote:

Hey Detlef,

Hope you are enjoying the conference!

Please call Frank directly (910-515-5952) as he has some important questions from the executive team.

Thank you,

Ben Kearns

Sent from my iPhone

On Jun 12, 2017, at 6:22 PM, Detlef Knappe <knappe@ncsu.edu> wrote:

Hi Ben,

I received your voice mail.

The only sample we have of CFPUA finished water is from August 18, 2014. GenX was 474 ng/L.

We have raw water samples for the following dates. These were composited daily samples.

Date	GenX (ng/L)
6/14/13	55.1
6/15/13	69.45
6/16/13	98.6
6/17/13	127.5
6/18/13	178
7/3/13	334
7/4/13	210.5
7/5/13	127

7/6/13	127
7/7/13	132.5
7/8/13	147
7/10/13	193.5
7/11/13	272
7/12/13	326
7/13/13	303
7/14/13	241.5
7/15/13	187.5
9/25/13	4560
9/26/13	3080
9/27/13	2200
9/28/13	1990
9/29/13	1575
9/30/13	863
10/1/13	567
10/2/13	577.5
10/4/13	368
10/5/13	369
10/6/13	334
10/7/13	354
10/8/13	307

10/9/13	327
10/10/13	275
10/11/13	266
10/13/13	305

In addition, we have a grab sample from the river from December 16, 2016 that was collected at Tar Heel. GenX was 172 ng/L.

I am at the AWWA conference in Philly, but I can call you tomorrow afternoon.

Best regards,
Dettef

--
Dettef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908
Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

--
Dettef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
<https://mail.google.com/mail/u/0/?ui=2&ik=79b349a7c3&view=pt&q=Beth.Eckert%40cftp...> 6/15/2017

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

--
Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering

North Carolina State University

Campus Box 7908

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

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This e-mail message has been scanned and cleared by MailMarshal SMTP.

milesfirm@gmail.com <milesfirm@gmail.com>

Wed, Jun 14, 2017 at 7:04 PM

To: Mike Brown <mike@capefearcommercial.com>, Jim Flechtner <jim.flechtner@cfpua.org>

Sent from my iPhone

Begin forwarded message:

From: George House <GHOUSE@brookspierce.com>

Date: June 14, 2017 at 5:42:09 PM EDT

To: Beth Eckert <Beth.Eckert@cfpua.org>, Linda Miles <milesfirm@gmail.com>

Cc: Frank Styers <Frank.Styers@cfpua.org>
Subject: Questions for Chemours

[Quoted text hidden]



Linda Miles <milesfirm@gmail.com>

Fwd: Voice mail

6 messages

Beth Eckert <Beth.Eckert@cfpua.org>

Wed, Jun 14, 2017 at 3:39 PM

To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>

FYI - additional information we got from Knapp late last night.

Beth Eckert

Begin forwarded message:

From: "Frank Styers" <Frank.Styers@cfpua.org>
To: "Jim Flechtner" <jim.flechtner@cfpua.org>
Cc: "Beth Eckert" <Beth.Eckert@cfpua.org>
Subject: FW: Voice mail

NC State email
↓
Chemours Info

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, June 13, 2017 11:50 PM
To: Frank Styers <Frank.Styers@cfpua.org>
Cc: John Malone <John.Malone@cfpua.org>; Beth Eckert <Beth.Eckert@cfpua.org>; Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Re: Voice mail

Hi Frank,

See my answers in CAPS below. Please let me know if clarifications are needed.

Thank you,

Detlef

On 6/13/17 2:04 PM, Frank Styers wrote:

Detlef,

I was wondering if you could answer the questions below:

- Did you originally expect that you would detect GenX in the samples and if so why?

MY EPA COLLABORATORS ANDREW LINDSTROM AND MARK

STRYNAR BEGAN IN 2012 TO SEARCH FOR THE IDENTITY OF THE COMPOUND THAT DUPONT INTRODUCED AS A REPLACEMENT FOR PFOA. THEIR WORK LED TO THE IDENTIFICATION OF GENX AND LATER THE OTHER ETHERS IN THE CAPE FEAR RIVER DOWNSTREAM OF THE CHEMOURS PLANT. THEIR WORK WAS PUBLISHED IN THE ATTACHED 2015 ARTICLE THAT APPEARED IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY.

MY STUDENTS BEGAN TO MEASURE GENX CONCENTRATIONS IN 2013, WHEN THE COMPANY WELLINGTON LABS INTRODUCED AN ANALYTICAL STANDARD FOR GENX (THEY CALL IT HFPO DIMER ACID - SEE http://www.well-labs.com/docs/hfpoda_m3hfpoda_20feb2013_wellington_reporter.pdf).

- The agreement for the GenX study was signed in the fall of 2015 but your samples were from 2013 and -14. Could you please explain the origin of the data, when were the samples were taken and when they were analyzed for Genx?

WE COLLECTED 34 SAMPLES BETWEEN JUNE 14, 2013 AND DECEMBER 2, 2013. THESE SAMPLES WERE COMPOSITED DAILY SAMPLES COLLECTED AT THE RAW WATER TAP OF THE SWEENEY PLANT. ON AUGUST 18, 2014, WE COLLECTED GRAB SAMPLES FROM THE RAW AND FINISHED WATER TAPS AS WELL AS AT SAMPLING POINTS WITHING THE SWEENEY WTP TO ASSESS THE PERFORMANCE OF INDIVIDUAL UNIT PROCESSES FOR PFAS CONTROL. ALL SAMPLES WERE ANALYZED WITHIN 7 DAYS OF RECEIPT OF THE SAMPLES AT NC STATE UNIVERSITY.

- Was there any testing performed to confirm the existence after 2014?

EPA COLLABORATORS COLLECTED SAMPLES AGAIN ON DECEMBER 16, 2016. A CAPE FEAR RIVER SAMPLE COLLECTED NEAR TAR HEEL EXHIBITED A GENX CONCENTRATION OF 172 NG/L.

- Was this run on 537, how did you identify GenX within this method and where did you get the GenX standard? If not what method was used?

WE USED AN IN-HOUSE LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY METHOD TO DETERMINE THE CONCENTRATIONS OF GENX. THE ANALYTICAL METHOD IS DESCRIBED IN THE ATTACHED SUPPORTING INFORMATION OF THE 2016 PAPER BY SUN. THE INFORMATION DESCRIBES THE MASS SPECTROMETER SETTINGS FOR THE IDENTIFICATION OF GENX AND THE OTHER ETHERS. THE GENX STANDARD WAS OBTAINED FROM WELLINGTON LABS AS DESCRIBED UNDER POINT 1

- We understand that you worked with EPA (in Research Triangle Park) to develop the test method. Is this correct?

YES

- Did you (NCSU) perform all of the tests, or did you send the samples to a lab to be tested?

AN NCSU STUDENT AND POSTDOC MEASURED THE GENX CONCENTRATIONS USING INSTRUMENTATION AT THE EPA LAB IN RESEARCH TRIANGLE PARK. NO SAMPLES WERE SENT TO OUTSIDE LABS.

- In the study (Figure 2-Fate of Genx through the plant) it appears this data represents results from a single sampling event that occurred August 2014, or is this graph produced from a conglomeration of multiple samples?

FIGURE 2 REPRESENTS THE RESULTS OF A SINGLE SAMPLING EVENT. GRAB SAMPLES WERE COLLECTED ON AUGUST 18, 2014.

- Have other samples been taken from the river or processes?

WE COLLECTED SAMPLES ALONG THE CAPE FEAR RIVER AND AT THE SWEENEY WTP AT THE END OF MAY 2017. THESE RESULTS ARE STILL PENDING.

- Can you further explain figure 2b?

FIGURE 2B ILLUSTRATES THAT IN ADDITION TO GENX (LABELED PFPrOPrA), HIGHLIGHTED IN THE DASHED OVAL, SIX ADDITIONAL PERFLUOROALKYL ETHER CARBOXYLIC ACIDS WERE DETECTED. NO ANALYTICAL STANDARDS WERE AVAILABLE FOR THE SIX ADDITIONAL COMPOUNDS. THEREFORE, WE CAN ONLY SHOW THE INSTRUMENT RESPONSE (PEAK AREA) FOR THESE COMPOUNDS. THREE COMPOUNDS (PFMOAA, PFO2HxA, and PFO3OA) HAD PEAK AREAS THAT WERE 2-113 TIMES GREATER THAN THAT OF PFPrOPrA. PEAK AREA IS PROPORTIONAL TO CONCENTRATION. THESE RESULTS THEREFORE SUGGEST THAT THE CONCENTRATIONS OF PFMOAA, PFO2HxA, and PFO3OA ARE SUBSTANTIALLY HIGHER THAN THE CONCENTRATION OF GENX. THE GENX CONCENTRATION IN THE FINISHED WATER WAS 474 NG/L ON AUGUST 18, 2014. ALSO, FIGURE 2B ILLUSTRATES THAT THE ADDITIONAL ETHER COMPOUNDS CANNOT BE REMOVED BY THE WATER TREATMENT PROCESSES EMPLOYED AT THE SWEENEY WTP.

Thanks,

Frank Styers

Office: (910) 332-6670

Cell (910) 515-5952

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, June 13, 2017 12:27 AM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Cc: Frank Styers <Frank.Styers@cfpua.org>; John Malone <John.Malone@cfpua.org>
Subject: Re: Voice mail

Frank,

I will call you tomorrow at 11:45.

Detlef

On 6/12/17 6:30 PM, Ben Kearns wrote:

Hey Detlef,

Hope you are enjoying the conference!

Please call Frank directly (910-515-5952) as he has some important questions from the executive team.

Thank you,

Ben Kearns

Sent from my iPhone

On Jun 12, 2017, at 6:22 PM, Detlef Knappe <knappe@ncsu.edu> wrote:

Hi Ben,

I received your voice mail.

The only sample we have of CFPUA finished water is from August 18, 2014. GenX was 474 ng/L.

We have raw water samples for the following dates. These were composited daily samples.

Date	GenX (ng/L)
6/14/13	55.1

6/15/13	69.45
6/16/13	98.6
6/17/13	127.5
6/18/13	178
7/3/13	334
7/4/13	210.5
7/5/13	127
7/6/13	127
7/7/13	132.5
7/8/13	147
7/10/13	193.5
7/11/13	272
7/12/13	326
7/13/13	303
7/14/13	241.5
7/15/13	187.5
9/25/13	4560
9/26/13	3080
9/27/13	2200
9/28/13	1990
9/29/13	1575
9/30/13	863

10/1/13	567
10/2/13	577.5
10/4/13	368
10/5/13	369
10/6/13	334
10/7/13	354
10/8/13	307
10/9/13	327
10/10/13	275
10/11/13	266
10/13/13	305

In addition, we have a grab sample from the river from December 16, 2016 that was collected at Tar Heel. GenX was 172 ng/L.

I am at the AWWA conference in Philly, but I can call you tomorrow afternoon.

Best regards,
Detlef

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and
Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
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Detlef Knappe
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Web page: <http://knappelab.wordpress.ncsu.edu/>

6 attachments

 **Ethers_Strynar_EST2015.pdf**
3102K

 **ATT00001.htm**
1K

 **Ethers_Strynar_EST2015SI.pdf**
2328K

 **ATT00002.htm**
1K

 **PFECA_Sun_ESTL2016_SI.pdf**
1182K

 **ATT00003.htm**
1K

milesfirm@gmail.com <milesfirm@gmail.com>
To: Beth Eckert <Beth.Eckert@cfpua.org>

Wed, Jun 14, 2017 at 3:44 PM

Come get me out of Jim's office and tell me what this Is this something critical we need to know

Sent from my iPhone

> On Jun 14, 2017, at 3:39 PM, Beth Eckert <Beth.Eckert@cfpua.org> wrote:
>
> <mime-attachment.html>
> <Ethers_Strynar_EST2015.pdf>
> <Ethers_Strynar_EST2015SI.pdf>
> <PFECA_Sun_ESTL2016_SI.pdf>

milesfirm@gmail.com <milesfirm@gmail.com>
To: George House <GHOUSE@brookspierce.com>

Wed, Jun 14, 2017 at 7:06 PM

Sent from my iPhone

Begin forwarded message:

From: Beth Eckert <Beth.Eckert@cfpua.org>
Date: June 14, 2017 at 3:39:24 PM EDT
To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>
Subject: Fwd: Voice mail

[Quoted text hidden]

3 attachments

 **Ethers_Strynar_EST2015.pdf**
3102K

 **Ethers_Strynar_EST2015SI.pdf**
2328K

 **PFECA_Sun_ESTL2016_SI.pdf**
1182K

George House <GHOUSE@brookspierce.com>
To: "milesfirm@gmail.com" <milesfirm@gmail.com>

Wed, Jun 14, 2017 at 8:52 PM

Talked to Mike. I assume you got my questions. You ok? Worried about you. When do you need me there tomorrow?

George House



t: 336.271.3114

f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

> On Jun 14, 2017, at 7:06 PM, "milesfirm@gmail.com" <milesfirm@gmail.com> wrote:

>

>

>

> Sent from my iPhone

>

> Begin forwarded message:

>

> From: Beth Eckert <Beth.Eckert@cfpua.org<mailto: Beth.Eckert@cfpua.org>>

> Date: June 14, 2017 at 3:39:24 PM EDT

> To: Linda Miles <milesfirm@gmail.com<mailto:milesfirm@gmail.com>>, GHOUSE
<GHOUSE@brookspierce.com<mailto:GHOUSE@brookspierce.com>>

> Subject: Fwd: Voice mail

>

> FYI - additional information we got from Knapp late last night.

>

> Beth Eckert

>

> Begin forwarded message:

>

> From: "Frank Styers" <Frank.Styers@cfpua.org<mailto: Frank.Styers@cfpua.org>>

> To: "Jim Flechtner" <jim.flechtner@cfpua.org<mailto:jim.flechtner@cfpua.org>>

> Cc: "Beth Eckert" <Beth.Eckert@cfpua.org<mailto: Beth.Eckert@cfpua.org>>

> Subject: FW: Voice mail

>

>

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Tuesday, June 13, 2017 11:50 PM

> To: Frank Styers <Frank.Styers@cfpua.org<mailto: Frank.Styers@cfpua.org>>

> Cc: John Malone <John.Malone@cfpua.org<mailto: John.Malone@cfpua.org>>; Beth Eckert
<Beth.Eckert@cfpua.org<mailto: Beth.Eckert@cfpua.org>>; Ben Kearns

<Ben.Kearns@cfpua.org<mailto: Ben.Kearns@cfpua.org>>

> Subject: Re: Voice mail

>

>

> Hi Frank,

>
> See my answers in CAPS below. Please let me know if clarifications are needed.
>
> Thank you,
>
> Detlef
>
> On 6/13/17 2:04 PM, Frank Styers wrote:
> Detlef,
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> I was wondering if you could answer the questions below:
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> * Did you originally expect that you would detect GenX in the samples and if so why?
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> MY EPA COLLABORATORS ANDREW LINDSTROM AND MARK STRYNAR BEGAN IN 2012 TO SEARCH FOR THE IDENTITY OF THE COMPOUND THAT DUPONT INTRODUCED AS A REPLACEMENT FOR PFOA. THEIR WORK LED TO THE IDENTIFICATION OF GENX AND LATER THE OTHER ETHERS IN THE CAPE FEAR RIVER DOWNSTREAM OF THE CHEMOURS PLANT. THEIR WORK WAS PUBLISHED IN THE ATTACHED 2015 ARTICLE THAT APPEARED IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY.
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> YES

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> * In the study (Figure 2-Fate of Genx through the plant) it appears this data represents results from a single sampling event that occurred August 2014, or is this graph produced from a conglomeration of multiple samples?
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>
>
>
> Thanks,
>
> Frank Styers
> Office: (910) 332-6670
> Cell (910) 515-5952
>
> From: Detlef Knappe [mailto:knappe@ncsu.edu]
> Sent: Tuesday, June 13, 2017 12:27 AM
> To: Ben Kearns <Ben.Kearns@cfpua.org><mailto:Ben.Kearns@cfpua.org>
> Cc: Frank Styers <Frank.Styers@cfpua.org><mailto:Frank.Styers@cfpua.org>; John Malone <John.Malone@cfpua.org><mailto:John.Malone@cfpua.org>
> Subject: Re: Voice mail
>
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> Frank,
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> I will call you tomorrow at 11:45.
>
> Detlef

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> Hope you are enjoying the conference!
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> Please call Frank directly (910-515-5952) as he has some important questions from the executive team.
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>
> Ben Kearns
> Sent from my iPhone
>
> [Quoted text hidden]
> E-mail: knappe@ncsu.edu<mailto:knappe@ncsu.edu>
>
> Web page: <http://knappelab.wordpress.ncsu.edu/>
>
>
>
>
> —
>
> Detlef Knappe
>
> Professor
>
> 319-E Mann Hall
>
> Department of Civil, Construction, and Environmental Engineering
>
> North Carolina State University
>
> Campus Box 7908
>
> Raleigh, NC 27695-7908
>
>
>
> Phone: 919-515-8791
>
> Fax: 919-515-7908
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> Web page: <http://knappelab.wordpress.ncsu.edu/>
> <Ethers_Strynar_EST2015.pdf>
> <Ethers_Strynar_EST2015SI.pdf>
> <PFECAs_Sun_ESTL2016_SI.pdf>

Confidentiality Notice:

The information contained in this e-mail transmittal is privileged and confidential intended for the addressee only. If you are neither the intended recipient nor the employee or agent responsible for delivering this e-mail to the intended recipient, any disclosure of this information in any way or taking of any action in reliance on this information is strictly prohibited. If you have received this e-mail in error, please notify the person transmitting the information immediately.

This e-mail message has been scanned and cleared by MailMarshal SMTP.

milesfirm@gmail.com <milesfirm@gmail.com>
To: George House <GHOUSE@brookspierce.com>

Wed, Jun 14, 2017 at 8:59 PM

Got the questions sent to mike. I don't know what time tomorrow. What is good for you. Going to have to work on resolution depending on what happens but could also due Friday morning early before 9 o clock meeting

Sent from my iPhone
[Quoted text hidden]

George House <GHOUSE@brookspierce.com>
To: "milesfirm@gmail.com" <milesfirm@gmail.com>

Wed, Jun 14, 2017 at 9:44 PM

What about 3pm?

George House



t: 336.271.3114

f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

[Quoted text hidden]



Linda Miles <milesfirm@gmail.com>

Fwd: chemours pres

13 messages

Beth Eckert <Beth.Eckert@cfpua.org>

Mon, Jun 12, 2017 at 6:42 PM

To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>, Frank Styers <Frank.Styers@cfpua.org>, Jim Flechtner <jim.flechtner@cfpua.org>, Carel Vandermeiden <Carel.Vandermeiden@cfpua.org>

PowerPoint from Chemours via Jim Gregson.

Beth Eckert

Begin forwarded message:

From: "Gregson, Jim" <jim.gregson@ncdenr.gov>
To: "Beth Eckert" <Beth.Eckert@cfpua.org>
Subject: Fwd: chemours pres

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section
Division of Water Resources
Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
Jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405

Email correspondence to and from this address is subject to the North Carolina Public Records Law and may be disclosed to third parties.

Begin forwarded message:

From: "Young, Sarah" <sarah.young@ncdenr.gov>
To: "Karoly, Cyndi" <cyndi.karoly@ncdenr.gov>, "Allen, Trent" <trent.allen@ncdenr.gov>, "Gregson, Jim" <jim.gregson@ncdenr.gov>
Cc: "Culpepper, Linda" <linda.culpepper@ncdenr.gov>
Subject: chemours pres

Sarah M. Young

Public Information Officer

N.C. Department of Environmental Quality

Division of Coastal Management

919-707-8604 office

sarah.young@ncdenr.gov

cid:image001.png@01D102AE.2E46C5
10

Email correspondence to and from this address is subject to the

North Carolina Public Records Law and may be disclosed to third parties.

2 attachments

 **Chemours GenX.pptx**
1749K

 **ATT00001.htm**
1K

Linda Miles <milesfirm@gmail.com>
To: George.house@brookspierce.com

Mon, Jun 12, 2017 at 7:13 PM

This was submitted by Chemours to DEQ. Chemours is in the manufacturing and discharge state now . They have agreed to do samples at our intake and submit to American Lab in Denver. The State is also going to take Samples. But the State claims they can not take action unless EPA sets a standard

[Quoted text hidden]

2 attachments

 **ATT00001.htm**
1K

 **Chemours GenX.pptx**
1749K

Mail Delivery Subsystem <mailer-daemon@googlemail.com>
To: milesfirm@gmail.com

Mon, Jun 12, 2017 at 7:13 PM



Message not delivered

There was a problem delivering your message to **George.house@brookspierce.com**. See the technical details below, or try resending in a few minutes.

The response was:

550 Rule imposed mailbox access for George.house@brookspierce.com refused

Final-Recipient: rfc822; George.house@brookspierce.com
Action: failed
Status: 5.0.0
Remote-MTA: dns; mail.brookspierce.com. (66.194.121.51, the server for the domain brookspierce.com.)
Diagnostic-Code: smtp; 550 Rule imposed mailbox access for George.house@brookspierce.com refused
Last-Attempt-Date: Mon, 12 Jun 2017 16:13:21 -0700 (PDT)

----- Forwarded message -----

From: Linda Miles <milesfirm@gmail.com>
To: George.house@brookspierce.com
Cc:
Bcc:

Date: Mon, 12 Jun 2017 19:13:19 -0400

Subject: Fwd: chemours pres

This was submitted by Chemours to DEQ. Chemours is in the manufacturing and discharge state now . They have agreed to do samples at our intake and submit to American Lab in Denver. The State is also going to take Samples. But the State claims they can not take action unless EPA sets a standard

----- Forwarded message -----

From: **Beth Eckert** <Beth.Eckert@cfpua.org>

Date: Mon, Jun 12, 2017 at 6:42 PM

Subject: Fwd: chemours pres

To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>, Frank Styers <Frank.Styers@cfpua.org>, Jim Flechtner <jim.flechtner@cfpua.org>, Carel Vandermeijden <Carel.Vandermeijden@cfpua.org>

PowerPoint from Chemours via Jim Gregson.

Beth Eckert

Begin forwarded message:

From: "Gregson, Jim" <jim.gregson@ncdenr.gov>
To: "Beth Eckert" <Beth.Eckert@cfpua.org>
Subjec — **Message truncated** —

Linda Miles <milesfirm@gmail.com>
To: GHOUSE <GHOUSE@brookspierce.com>

Mon, Jun 12, 2017 at 7:14 PM

presentation from Chemours to State

—— Forwarded message ——

From: **Beth Eckert** <Beth.Eckert@cfpua.org>

Date: Mon, Jun 12, 2017 at 6:42 PM

Subject: Fwd: chemours pres

To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>, Frank Styers <Frank.Styers@cfpua.org>, Jim Flechtner <jim.flechtner@cfpua.org>, Carel Vandermeijden <Carel.Vandermeijden@cfpua.org>

[Quoted text hidden]

2 attachments

 **ATT00001.htm**
1K

 **Chemours GenX.pptx**
1749K

Linda Miles <milesfirm@gmail.com>
To: GHOUSE <GHOUSE@brookspierce.com>

Mon, Jun 12, 2017 at 7:15 PM

State said they could only get voluntary compliance until EPA set standards. Just got out of meetings

[Quoted text hidden]

George House <GHOUSE@brookspierce.com>
To: Linda Miles <milesfirm@gmail.com>
Cc: "Beth Eckert (Beth.Eckert@cfpua.org)" <Beth.Eckert@cfpua.org>

Tue, Jun 13, 2017 at 8:17 AM

I have read this several times. Are they saying they have 5 or more different GenX waste streams? As you note from my discussion yesterday, I think the Consent Order mandates they sample each process wastewater stream, not the whole at outfall 002. This discussion may be in the App which I will read as I drive down.

George House



t: 336.271.3114

f: 336.232.9114

2000 Renaissance Plaza
230 North Elm Street
Greensboro, NC 27401
P.O. Box 26000 (27420)

From: Linda Miles [mailto:milesfirm@gmail.com]
Sent: Monday, June 12, 2017 7:15 PM
To: George House <GHOUSE@brookspierce.com>
Subject: Fwd: chemours pres

presentation from Chemours to State

----- Forwarded message -----

From: Beth Eckert <Beth.Eckert@cfpua.org>
Date: Mon, Jun 12, 2017 at 6:42 PM
Subject: Fwd: chemours pres
To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>, Frank Styers <Frank.Styers@cfpua.org>, Jim Flechtner <jim.flechtner@cfpua.org>, Carel Vandermeiden <Carel.Vandermeiden@cfpua.org>

PowerPoint from Chemours via Jim Gregson.

Beth Eckert

Begin forwarded message:

From: "Gregson, Jim" <jim.gregson@ncdenr.gov>
To: "Beth Eckert" <Beth.Eckert@cfpua.org>
Subject: Fwd: chemours pres

Jim Gregson

Regional Supervisor

Water Quality Regional Operations Section

Division of Water Resources

Department of Environmental Quality

910.796.7215 Reception Desk

910.796.7386 Direct

910.350.2004 Fax

Jim.gregson@ncdenr.gov

Wilmington Regional Office

127 Cardinal Drive Ext

Wilmington, NC 28405

*Email correspondence to and from this address is subject to the
North Carolina Public Records Law and may be disclosed to third parties.*

Begin forwarded message:

From: "Young, Sarah" <sarah.young@ncdenr.gov>
To: "Karoly, Cyndi" <cyndi.karoly@ncdenr.gov>, "Allen, Trent"
<trent.allen@ncdenr.gov>, "Gregson, Jim" <jim.gregson@ncdenr.gov>
Cc: "Culpepper, Linda" <linda.culpepper@ncdenr.gov>
Subject: chemours pres

Sarah M. Young

Public Information Officer

N.C. Department of Environmental Quality

Division of Coastal Management

919-707-8604 office

sarah.young@ncdenr.gov

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This e-mail message has been scanned and cleared by MailMarshal SMTP.

milesfirm@gmail.com <milesfirm@gmail.com>
To: patricia.kusek@lpl.com

Tue, Jun 13, 2017 at 3:53 PM

Sent from my iPhone

Begin forwarded message:

From: George House <GHOUSE@brookspierce.com>
Date: June 13, 2017 at 8:17:56 AM EDT
To: Linda Miles <milesfirm@gmail.com>
Cc: "Beth Eckert (Beth.Eckert@cfpua.org)" <Beth.Eckert@cfpua.org>
Subject: RE: chemours pres

[Quoted text hidden]

milesfirm@gmail.com <milesfirm@gmail.com>
To: ww@woodywhitelaw.com

Tue, Jun 13, 2017 at 4:22 PM

Sent from my iPhone

Begin forwarded message:

From: George House <GHOUSE@brookspierce.com>
Date: June 13, 2017 at 8:17:56 AM EDT
To: Linda Miles <milesfirm@gmail.com>
Cc: "Beth Eckert (Beth.Eckert@cfpua.org)" <Beth.Eckert@cfpua.org>
Subject: RE: chemours pres

[Quoted text hidden]

milesfirm@gmail.com <milesfirm@gmail.com>
To: Donna Pope <Donna.Pope@cfpua.org>

Tue, Jun 13, 2017 at 4:23 PM

Can you print 3 copies please

Sent from my iPhone

Begin forwarded message:

From: George House <GHOUSE@brookspierce.com>
Date: June 13, 2017 at 8:17:56 AM EDT
To: Linda Miles <milesfirm@gmail.com>
Cc: "Beth Eckert (Beth.Eckert@cfpua.org)" <Beth.Eckert@cfpua.org>
Subject: RE: chemours pres

[Quoted text hidden]

Linda Miles <milesfirm@gmail.com>
To: Donna Pope <Donna.pope@cfpua.org>

Tue, Jun 13, 2017 at 4:33 PM

----- Forwarded message -----

From: Beth Eckert <Beth.Eckert@cfpua.org>
Date: Mon, Jun 12, 2017 at 6:42 PM
Subject: Fwd: chemours pres
To: Linda Miles <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>, Frank Styers <Frank.Styers@cfpua.org>, Jim Flechtner <jim.flechtner@cfpua.org>, Carel Vandermeiden <Carel.Vandermeiden@cfpua.org>

[Quoted text hidden]

2 attachments

 **ATT00001.htm**
1K

 **Chemours GenX.pptx**
1749K

Woody White <ww@woodywhitelaw.com>
To: "milesfirm@gmail.com" <milesfirm@gmail.com>

Tue, Jun 13, 2017 at 5:17 PM

Please resend.

It did not attach.

Woody White

Woody White Law PLLC

2004 Eastwood Rd. – Suite 201

Wilmington, N.C. 28403

www.woodywhitelaw.com

Office: 910-239-9585

Fax: 910-679-4522

*Board Certified Specialist in State/Federal Criminal Law

*New Hanover County Commissioner

From: milesfirm@gmail.com [mailto:milesfirm@gmail.com]
Sent: Tuesday, June 13, 2017 4:22 PM
To: Woody White
Subject: Fwd: chemours pres

[Quoted text hidden]

milesfirm@gmail.com <milesfirm@gmail.com>
To: Woody White <ww@woodywhitelaw.com>

Tue, Jun 13, 2017 at 8:49 PM

Trying again. I printed this though and gave you a copy in the materials

Let me know if it doesn't go through

Sent from my iPhone

Begin forwarded message:

From: Linda Miles <milesfirm@gmail.com>
Date: June 12, 2017 at 7:14:49 PM EDT
To: GHOUSE <GHOUSE@brookspierce.com>
Subject: Fwd: chemours pres

[Quoted text hidden]

 **Chemours GenX.pptx**
1749K

Woody White <ww@woodywhitelaw.com>
To: "milesfirm@gmail.com" <milesfirm@gmail.com>

Tue, Jun 13, 2017 at 8:50 PM

Got it.
Thanks Linda

Woody White
Www. Woodywhitelaw.com
910-239-9585

> On Jun 13, 2017, at 8:49 PM, "milesfirm@gmail.com" <milesfirm@gmail.com> wrote:

>

> Trying again. I printed this though and gave you a copy in the materials

>

>

> Let me know if it doesn't go through

>

> Sent from my iPhone

>

> Begin forwarded message:

>

> From: Linda Miles <milesfirm@gmail.com<mailto:milesfirm@gmail.com>>

> Date: June 12, 2017 at 7:14:49 PM EDT

> To: GHOUSE <GHOUSE@brookspierce.com<mailto:GHOUSE@brookspierce.com>>

> Subject: Fwd: chemours pres

>

> presentation from Chemours to State

> ----- Forwarded message -----

> From: Beth Eckert <Beth.Eckert@cfpua.org<mailto:Beth.Eckert@cfpua.org>>

> Date: Mon, Jun 12, 2017 at 6:42 PM

> Subject: Fwd: chemours pres

> To: Linda Miles <milesfirm@gmail.com<mailto:milesfirm@gmail.com>>, GHOUSE
<GHOUSE@brookspierce.com<mailto:GHOUSE@brookspierce.com>>, Frank Styers
<Frank.Styers@cfpua.org<mailto:Frank.Styers@cfpua.org>>, Jim Flechtner
<jim.flechtner@cfpua.org<mailto:jim.flechtner@cfpua.org>>, Carel Vandermeiden
<Carel.Vandermeiden@cfpua.org<mailto:Carel.Vandermeiden@cfpua.org>>

>

>

> PowerPoint from Chemours via Jim Gregson.

>

> Beth Eckert

>

> Begin forwarded message:

>

> From: "Gregson, Jim" <jim.gregson@ncdenr.gov<mailto:jim.gregson@ncdenr.gov>>

> To: "Beth Eckert" <Beth.Eckert@cfpua.org<mailto:Beth.Eckert@cfpua.org>>

> Subject: Fwd: chemours pres

>

>

>

> Jim Gregson

> Regional Supervisor

> Water Quality Regional Operations Section

> Division of Water Resources

> Department of Environmental Quality

>

> 910.796.7215<tel:910.796.7215> Reception Desk

> 910.796.7386<tel:910.796.7386> Direct

> 910.350.2004<tel:910.350.2004> Fax

> Jim.gregson@ncdenr.gov<mailto:Jim.gregson@ncdenr.gov>

>

> Wilmington Regional Office


> 127 Cardinal Drive Ext

> Wilmington, NC 28405

>

> [cid:]
>
> Email correspondence to and from this address is subject to the
> North Carolina Public Records Law and may be disclosed to third parties.
>
> Begin forwarded message:
>
> From: "Young, Sarah" <sarah.young@ncdenr.gov<mailto:sarah.young@ncdenr.gov>>
> To: "Karoly, Cyndi" <cyndi.karoly@ncdenr.gov<mailto:cyndi.karoly@ncdenr.gov>>, "Allen, Trent"
<trent.allen@ncdenr.gov<mailto:trent.allen@ncdenr.gov>>, "Gregson, Jim"
<jim.gregson@ncdenr.gov<mailto:jim.gregson@ncdenr.gov>>
> Cc: "Culpepper, Linda" <linda.culpepper@ncdenr.gov<mailto:linda.culpepper@ncdenr.gov>>
> Subject: chemours pres
>
>
>
> Sarah M. Young
> Public Information Officer
> N.C. Department of Environmental Quality
> Division of Coastal Management
>
> 919-707-8604<tel:(919)%20707-8604> office
> sarah.young@ncdenr.gov<mailto:sarah.young@ncdenr.gov>
>
>
> [cid:image001.png@01D102AE.2E46C510]
>
> Email correspondence to and from this address is subject to the
> North Carolina Public Records Law and may be disclosed to third parties.
>
>
> <Chemours GenX.pptx>

DENR/DWQ
FACT SHEET FOR NPDES PERMIT DEVELOPMENT
 NPDES No. NC0003573

Facility Information			
Applicant/Facility Name:	E.I. DuPont de Nemours & Co – DuPont Fayetteville Works		
Applicant Address:	22828 NC Hwy 87W, Fayetteville, NC 28306-7332		
Facility Address:	22828 NC Hwy 87W, Fayetteville, NC 28306-7332		
Permitted Flow (MGD):	2 MGD – WWTP (Outfall 001 -external)		
Type of Waste:	Industrial		
Facility Classification:	III		
Permit Status:	Renewal		
County:	Bladen		
Miscellaneous			
Receiving Stream:	Cape Fear River	Regional Office:	Fayetteville
Stream Classification:	C, WS-IV	USGS Quad:	Duart
303(d) Listed?	No	Permit Writer:	Sergei Chernikov
Basin/Subbasin:	03-06-16	Date:	08/09/2011
Drainage Area (mi ²):	4790	 Lat. 34° 50' 18" N Long. 78° 49' 47" W	
Summer 7Q10 (cfs)	791		
Winter 7Q10 (cfs):			
30Q2 (cfs)			
Average Flow (cfs):	5676		
IWC (%):	3.3 %		

Summary:

E.I. DuPont de Nemours & Co submitted a permit renewal application on May 2, 2011 for the renewal of its NPDES permit. The DuPont Fayetteville Works manufacturing facility includes the Butacite® plant, the Nafion® plant, the Teflon® plant, and the APFO plant. A new process was added in 2011 to produce Polyvinyl Fluoride (PVF) resins. The process wastewaters generated from the new facility will be treated in the existing treatment plant.

Manufacturing Facilities:

Buticite® Manufacturing

- DuPont™ Buticite® Interlayer plastic sheeting – This is the final product used in safety glass such as automobile windshields.

Butacite® is manufactured in large rolls and shipped out in refrigerated trucks to glass manufacturers. The refrigeration is a requirement as butacite sticks to itself at temperatures above 60°F.

- Polyvinyl butyral (PVB) resin - the resin is shipped to other DuPont facilities for final processing.

Wastewaters generated at this facility are treated in the on-site wastewater treatment plant.

Nafion® Manufacturing

Five products are manufactured at the Nafion® manufacturing facility:

- DuPont™ Nafion® membrane – a plastic film used in the chloroalkali industry and in electrochemical fuel cells;

- Nafion® resins – ultimately extruded into a finished film;
- Nafion® solution – generated during the production of resin;
- FLPR vinyl ether monomers – shipped to other DuPont locations to produce various fluorochemical products such as DuPont™ Teflon®.
- HFPO monomers – shipped to other DuPont locations to produce various fluorochemical products such as DuPont™ Teflon®.

Wastewaters generated at this facility are neutralized and treated in the on-site WWTP.

PPA Manufacturing

The processing aids produced in this units are used to produce fluoropolymers and fluorinated telomers that are shipped to other DuPont facilities. This facility was started up in November 2002.

Wastewaters generated in this process are collected and shipped off-site for disposal.

Sentry Glass Plus® Manufacturing

DuPont™ Sentry Glass Plus® - this is an ionoplast interlayer laminate used for laminated safety glass in side, rear, and overhead automobile windows. It is also used in architectural applications desiring safety glass.

This manufacturing process started in June 2005. No process wastewaters are generated from this process. Non-contact cooling water is discharged to Outfall 002.

Proposed PVF-3 Manufacturing

This facility will produce Polivinyll fluoride resins (PVF) and is expected to start production in 2013. The manufacturing facility will be located near the existing PVF-1 and PVF-2 manufacturing processes. PVF is used in DuPont™ Tedlar® fluoropolymer film manufactured at other DuPont facilities. Tedlar® is used in the photovoltaic industry in photovoltaic cells and the aircraft industry for interior cabin surfaces, as well as other uses.

The PVF-1 facility began operation during September 2007, the PVF-2 facility began operation during June 2010. Process wastewater generated from this manufacturing facility is treated in the WWTP. Non-contact cooling water, condensate and stormwater will be discharged to Outfall 002.

Wastewater Treatment:

Process wastewaters and stormwater from process areas are collected in sumps in the respective manufacturing areas and conveyed via gravity sewers to the wastewater treatment plant. Sanitary sewage is conveyed separately to the WWTP.

The treatment system discharges through Outfall 001 to the main discharge channel. Non-process cooling waters and stormwater are conveyed to ditches and discharged to the main discharge channel. The combined flows are discharged through Outfall 002 to the Cape Fear River below Lock and Dam #3.

Effluent Guidelines:

DuPont's Fayetteville Works is regulated under the Organic Chemicals, Plastics and Synthetic Fibers Category, 40 CFR 414 Subpart D. These guidelines apply to products manufactured under SIC codes 2869 and 2821. SIC code 2869 includes Nafion® solution, Vinyl Ether and HFPO monomers manufacturing. SIC code 2821 includes Teflon® resin, polyvinyl fluoride resin, polyvinyl butyral resin and Nafion® resin manufacturing. Manufacturing of Nafion membrane, Butacite® sheeting and Sentry Glass plus are classified as SIC code 3081 which is not regulated by the OCPSF guidelines.

Regulated process flow for Outfall 001 is approximately 0.9 MGD. This flow includes the flow from PVF manufacturing process.

EG limits - Subpart D - Thermoplastic Resins, 414.41

Limits are calculated by multiplying the allocation from the effluent guidelines by 8.34 (conversion factor) and by OCPSF process flow.

Parameter	Effluent Limitations (concentration)		Effluent Limitations (Mass limits)		Domestic WW (mass limits)		Proposed limits (mass limits)	
	Maximum Daily (mg/l)	Maximum Monthly Average (mg/l)	Daily Maximum (lb/day)	Monthly Average (lb/day)	Daily Maximum (lb/day)	Monthly Average (lb/day)	Daily Maximum (lb/day)	Monthly Average (lb/day)
BOD	64	24	481.7	180.6	3	2	484.7	182.6
TSS	130	40	978.5	301.1	3	2	981.5	303.1

Process flow - 0.9025 MGD.

Compliance Summary:

During the review period (2007-2011) the facility did not receive any Notices of Violation.

Whole Effluent Toxicity - The permit requires a quarterly chronic test at 3.3 %. The facility passed all the tests during the previous permit term (please see attached).

Reasonable Potential Analysis (RPA):

The RPA was conducted for F, please see attached.

Instream data review:

There are monitoring stations in the Cape Fear River upstream (B8301000) and downstream (B8302000) of the discharge. Data from the monitoring stations indicates no noticeable impact from the discharge.

SUMMARY OF PROPOSED CHANGES:

- One clarifier was added to the description of the treatment facility.
- The permit limits have recalculated based on the latest OCPSF production information in accordance with the 40 CFR 414 Subpart D.
- The limits for Cr, Cu, CN, Pb, Ni, and Zn were added to the permit in accordance with the 40 CFR 414 Subpart D.
- The limit for F was removed from the permit based on the statistical analysis of the effluent data and the monitoring was reduced to quarterly. The instream monitoring for F was removed from the permit.

PROPOSED SCHEDULE FOR PERMIT ISSUANCE

Draft Permit to Public Notice:

August 31, 2011

Permit Scheduled to Issue:

October 24, 2011

NPDES DIVISION CONTACT

If you have questions regarding any of the above information or on the attached permit, please contact Sergei Chernikov at (919) 807-6393.

CHANGES IN THE FINAL PERMIT:

- Tertiary filters were removed from the description of the wastewater treatment facilities.
- Classification of the receiving stream was changes to Class C, WS-IV.
- Cooling tower blowdown was added to the description of waste streams.
- Chronic toxicity monitoring requirement was moved to the Outfall 002.

North Carolina Department of Environmental Quality

Pat McCrory
Governor

Donald R. van der Vaart
Secretary

October 28, 2015

Mr. Michael Johnson, PE
Environmental Manager
The Chemours Company FC, LLC
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

Subject: NPDES Permit Modification
Permit NC0003573
Ownership Change
Bladen County
Class II Facility

Dear Mr. Johnson:

Division personnel have reviewed and approved your request for permit modification of the subject permit, to reflect new facility ownership effective July 1, 2015. Accordingly, we are enclosing modified pages to reflect the new ownership. Please insert these modified pages into your current permit. A complete review of this permit will be conducted with your next permit renewal in 2016. This permit modification is issued pursuant to the requirements of North Carolina General Statute 143-215.1 and the Memorandum of Agreement between North Carolina and the U.S. Environmental Protection Agency dated October 15, 2007 (or as subsequently amended). If you have any questions, feel free to contact me at 919-807-6390 or via email at tom.belnick@ncdenr.gov.

Sincerely,

S. Jay Zimmerman, P.G.
Director, Division of Water Resources

cc: NPDES Files
Central Files

Ecopy:
EPA Region 4
DWR Fayetteville Regional Office/Water Quality
DWR Aquatic Toxicology

1601 Mail Service Center, Raleigh, North Carolina 27699-1601
Phone: 919-707-8600 \ Internet: www.ncdenr.gov

**STATE OF NORTH CAROLINA
DEPARTMENT OF ENVIRONMENTAL QUALITY
DIVISION OF WATER RESOURCES**

NPDES PERMIT

**TO DISCHARGE WASTEWATER UNDER THE
NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM**

In compliance with the provisions of North Carolina General Statute 143-215.1, other lawful standards and regulations promulgated and adopted by the North Carolina Environmental Management Commission, and the Federal Water Pollution Control Act, as amended,

The Chemours Company FC, LLC

is hereby authorized to discharge wastewater and stormwater from a facility located at

**Chemours Company- Fayetteville Works
22828 NC Highway 87 W
Fayetteville
Bladen County**

to receiving waters designated as the Cape Fear River in the Cape Fear River Basin in accordance with effluent limitations, monitoring requirements, and other conditions set forth in Parts I, II, III, and IV hereof.

The permit modification shall become effective July 1, 2015.

This permit and the authorization to discharge shall expire at midnight on October 31, 2016.

Signed this day October 28, 2015.

S. Jay Zimmerman, P.G.
Director, Division of Water Resources
By Authority of the Environmental Management Commission

SUPPLEMENT TO PERMIT COVER SHEET

All previous NPDES Permits issued to this facility, whether for operation or discharge are hereby revoked, and as of this issuance, any previously issued permit bearing this number is no longer effective. Therefore, the exclusive authority to operate and discharge from this facility arises under the permit conditions, requirements, terms, and provisions included herein.

The Chemours Company FC, LLC

is hereby authorized to:

1. Continue to operate existing wastewater treatment facilities consisting of:
 - equalization;
 - neutralization;
 - aerated pre-digester tank;
 - nutrient feed system;
 - aeration tank;
 - three clarifiers;
 - effluent flow measurement;
 - DAF unit;
 - rotary filter for sludge thickening;
 - sludge pump;
 - sludge filter press; and
 - steam heated sludge dryers.
2. Discharge treated process wastewater from Butacite®, Nafion®, SentryGlas®, and PVF (polyvinyl fluoride resin), process stormwater, sanitary wastewater, and co-neutralized regenerate from said treated facilities through internal outfall 001;
3. Discharge stormwater, non-contact cooling water, boiler blowdown and condensate, cooling tower blowdown, and treated wastewater effluent from 001, through outfall 002 at the location specified on the attached map into the Cape Fear River, a class C, WS-IV water in the Cape Fear River Basin.

A. (1) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee is authorized to discharge from **Outfall 001**. Such discharges shall be limited and monitored by the Permittee as specified below:

PARAMETER	EFFLUENT LIMITATIONS		MONITORING REQUIREMENTS		
	Monthly Average	Daily Maximum	Measurement Frequency	Sample Type	Sample Location
Flow (MGD)	2.0		Continuous	Recording	Effluent
BOD ₅ , 20° C	182.6 lbs/day	484.7 lbs/day	3/Week	Composite	Effluent
Total Suspended Solids	303.1 lbs/day	981.5 lbs/day	3/Week	Composite	Effluent
Temperature			Weekly	Grab	Effluent
Oil & Grease			Monthly	Grab	Effluent
pH	Between 6.0 and 9.0 Standard Units		3/Week	Grab	Effluent
40 CFR 414 Subpart I	See Condition A. (2)				

THERE SHALL BE NO DISCHARGE OF FLOATING SOLIDS OR VISIBLE FOAM IN OTHER THAN TRACE AMOUNTS.

A. (2) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS - SUBPART I

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee shall comply with the limitations and monitoring frequencies established below at outfall 001:

PARAMETER	EFFLUENT LIMITATIONS	MONITORING REQUIREMENTS
-----------	----------------------	-------------------------

	Monthly Average ¹	Daily Maximum ¹	Measurement Frequency	Sample Type	Sample Location
Acenaphthene	0.166	0.444	See Note 2	Grab	Effluent
Acenaphthylene	0.166	0.444	See Note 2	Grab	Effluent
Acrylonitrile	0.723	1.821	See Note 2	Grab	Effluent
Anthracene	0.166	12.8 ug/L	See Note 2	Grab	Effluent
Benzene	0.278	1.024	See Note 2	Grab	Effluent
Benzo(a)anthracene	0.166	0.444	See Note 2	Grab	Effluent
3,4-Benzofluoranthene	0.173	0.459	See Note 2	Grab	Effluent
Benzo(k)fluoranthene	0.166	0.444	See Note 2	Grab	Effluent
Benzo(a)pyrene	0.173	0.459	See Note 2	Grab	Effluent
Bis(2-ethylhexyl) phthalate	0.775	2.100	See Note 2	Grab	Effluent
Carbon Tetrachloride	0.135	0.286	See Note 2	Grab	Effluent
Chlorobenzene	0.113	0.211	See Note 2	Grab	Effluent
Chloroethane	0.783	2.017	See Note 2	Grab	Effluent
Chloroform	0.158	0.346	See Note 2	Grab	Effluent
2-Chlorophenol	0.233	0.738	See Note 2	Grab	Effluent
Chrysene	0.166	0.444	See Note 2	Grab	Effluent
Di-n-butyl phthalate	0.203	0.429	See Note 2	Grab	Effluent
1,2-Dichlorobenzene	0.580	1.227	See Note 2	Grab	Effluent
1,3-Dichlorobenzene	0.233	0.331	See Note 2	Grab	Effluent
1,4-Dichlorobenzene	0.113	0.211	See Note 2	Grab	Effluent
1,1-Dichloroethane	0.166	0.444	See Note 2	Grab	Effluent
1,2-Dichloroethane	0.512	1.588	See Note 2	Grab	Effluent
1,1-Dichloroethylene	0.120	0.188	See Note 2	Grab	Effluent
1,2-trans-Dichloroethylene	0.158	0.406	See Note 2	Grab	Effluent
2,4-Dichlorophenol	0.294	0.843	See Note 2	Grab	Effluent
1,2-Dichloropropane	1.152	1.731	See Note 2	Grab	Effluent
1,3-Dichloropropylene	0.218	0.331	See Note 2	Grab	Effluent
Diethyl phthalate	0.610	1.528	See Note 2	Grab	Effluent
2,4-Dimethylphenol	0.135	0.271	See Note 2	Grab	Effluent
Dimethyl phthalate	0.143	0.354	See Note 2	Grab	Effluent
4,6-Dinitro-o-cresol	0.587	2.085	See Note 2	Grab	Effluent
2,4-Dinitrophenol	0.534	0.926	See Note 2	Grab	Effluent
2,4-Dinitrotoluene	0.851	2.145	See Note 2	Grab	Effluent
2,6-Dinitrotoluene	1.919	12.3 ug/L	See Note 2	Grab	Effluent
Ethylbenzene	0.241	0.813	See Note 2	Grab	Effluent

A. (2) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS - SUBPART I (CONTUNUED)

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee shall comply with the limitations and monitoring frequencies established below at outfall 001:

PARAMETER	EFFLUENT LIMITATIONS	MONITORING REQUIREMENTS
-----------	----------------------	-------------------------

	Monthly Average ¹	Daily Maximum ¹	Measurement Frequency	Sample Type	Sample Location
Fluoranthene	0.188	28.2 ug/L	See Note 2	Grab	Effluent
Fluorene	0.166	0.444	See Note 2	Grab	Effluent
Hexachlorobenzene	0.113	0.5 µg/L	Annually ³	Grab	Effluent
Hexachlorobutadiene	0.151	0.369	See Note 2	Grab	Effluent
Hexachloroethane	0.158	0.406	See Note 2	Grab	Effluent
Methyl Chloride	0.647	1.430	See Note 2	Grab	Effluent
Methylene Chloride	0.301	0.670	See Note 2	Grab	Effluent
Naphthalene	0.166	0.444	See Note 2	Grab	Effluent
Nitrobenzene	0.203	0.512	See Note 2	Grab	Effluent
2-Nitrophenol	0.309	0.519	See Note 2	Grab	Effluent
4-Nitrophenol	0.542	0.933	See Note 2	Grab	Effluent
Phenanthrene	0.166	0.444	See Note 2	Grab	Effluent
Phenol	0.113	0.196	See Note 2	Grab	Effluent
Pyrene	0.188	0.504	See Note 2	Grab	Effluent
Tetrachloroethylene	0.166	0.422	See Note 2	Grab	Effluent
Toluene	0.196	0.602	See Note 2	Grab	Effluent
1,2,4-Trichlorobenzene	0.512	1.054	See Note 2	Grab	Effluent
1,1,1-Trichloroethane	0.158	0.406	See Note 2	Grab	Effluent
1,1,2-Trichloroethane	0.158	0.406	See Note 2	Grab	Effluent
Trichloroethylene	0.158	0.406	See Note 2	Grab	Effluent
Vinyl Chloride	0.783	2.017	See Note 2	Grab	Effluent
Total Chromium	8.355	20.849	Annually	Grab	Effluent
Total Copper	10.914	25.441	Annually	Grab	Effluent
Total Cyanide	3.161	9.032	See Note 2	Grab	Effluent
Total Lead	2.409	5.194	See Note 2	Grab	Effluent
Total Nickel	12.720	29.957	Annually	Grab	Effluent
Total Zinc	7.903	19.645	Annually	Grab	Effluent

Notes:

1. All units are lbs/day unless otherwise noted.
2. Monitoring for the specified parameters has been waived based on a demonstration made by the Permittee in accordance with 40 CFR 122.44(a)(2)(i). This waiver is good only for the term of the permit. Please note that any exceedence of the effluent limitations found herein shall be considered a permit violation subject to appropriate enforcement action.
3. The most sensitive analytical method available shall be employed for determining the presence of hexachlorobenzene in the effluent.

A. (3) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee is authorized to discharge from **Outfall 002 (boiler blowdown, once-through cooling water, and treated wastewater from outfall 001)** Such discharges shall be limited and monitored by the Permittee as specified below:

PARAMETER	EFFLUENT LIMITATIONS	MONITORING REQUIREMENTS
-----------	----------------------	-------------------------

	Monthly Average	Daily Maximum	Measurement Frequency	Sample Type	Sample Location ¹
Flow (MGD)			Continuous	Recording	Effluent or Influent
Temperature, °C	See Note 2		Daily ³	Grab	Effluent, Upstream, Downstream
BOD ₅ , 20°C			Quarterly	Composite	Effluent
COD			Quarterly	Composite	Effluent
Fluoride (ug/L)			Quarterly	Grab	Effluent
Dissolved Oxygen			Weekly	Grab	Upstream, Downstream
PFOA ⁴			Monthly	Grab	Effluent
Total Phosphorus			Monthly	Composite	Effluent
Total Nitrogen (NO ₂ +NO ₃ +TKN)			Monthly	Composite	Effluent
Conductivity			Weekly	Grab	Upstream, Downstream
Chronic Toxicity	See Note 5		Quarterly	Composite	Effluent
pH	Between 6.0 and 9.0 Standard Units		3/Week	Grab	Effluent

Notes:

- Upstream shall be at the Permittee's river pump station; downstream shall be at the boat ramp approximately 4500 feet downstream at Prospect Hall Landing.
As a participant in the Middle Cape Fear River Basin Association, the instream monitoring requirements as stated above are waived. Should your membership in the agreement be terminated, you shall notify the Division immediately and the instream monitoring requirements specified in your permit shall be reinstated.
- The temperature of the effluent shall be such as not to cause an increase in the temperature of the receiving stream of more than 2.8°C and in no case cause the ambient water temperature to exceed 32°C.
- Daily shall be defined as every day except Saturdays, Sundays, and legal holidays. Instream temperature sampling shall be conducted weekly.
- PFOA (Perfluorooctanoic acid) - The Cape Fear River water intake may be sampled for PFOA on a monthly basis and reported as an upstream parameter in DWQ Form - MR-3.
- Chronic Toxicity (*Ceriodaphnia*) P/F @ 3.3% February, May, August, November; see condition A. (4) of this permit. The compliance monitoring point for chronic toxicity shall be downstream of the confluence of outfall 001 and 002.

THERE SHALL BE NO DISCHARGE OF FLOATING SOLIDS OR VISIBLE FOAM IN OTHER THAN TRACE AMOUNTS.

A. (4) CHRONIC TOXICITY PERMIT LIMIT (QUARTERLY) – OUTFALL 002

The effluent discharge shall at no time exhibit observable inhibition of reproduction or significant mortality to *Ceriodaphnia dubia* at an effluent concentration of 3.3%.

The permit holder shall perform at a minimum, quarterly monitoring using test procedures outlined in the "North Carolina *Ceriodaphnia* Chronic Effluent Bioassay Procedure," Revised February 1998, or subsequent versions or "North Carolina Phase II Chronic Whole Effluent Toxicity Test Procedure" (Revised-February 1998) or subsequent versions. The tests will be performed during the months of February, May, August, and November. Effluent sampling for this testing shall be performed at the NPDES permitted final effluent discharge below all treatment processes.

If the test procedure performed as the first test of any single quarter results in a failure or ChV below the permit limit, then multiple-concentration testing shall be performed at a minimum, in each of the two following months as described in "North Carolina Phase II Chronic Whole Effluent Toxicity Test Procedure" (Revised-February 1998) or subsequent versions.

The chronic value for multiple concentration tests will be determined using the geometric mean of the highest concentration having no detectable impairment of reproduction or survival and the lowest concentration that does have a detectable impairment of reproduction or survival. The definition of "detectable impairment," collection methods, exposure regimes, and further statistical methods are specified in the "North Carolina Phase II Chronic Whole Effluent Toxicity Test Procedure" (Revised-February 1998) or subsequent versions.

All toxicity testing results required as part of this permit condition will be entered on the Effluent Discharge Monitoring Form (MR-1) for the months in which tests were performed, using the parameter code TGP3B for the pass/fail results and THP3B for the Chronic Value. Additionally, DWQ Form AT-3 (original) is to be sent to the following address:

Attention: Environmental Sciences Section
North Carolina Division of Water Quality
1621 Mail Service Center
Raleigh, North Carolina 27699-1621

Completed Aquatic Toxicity Test Forms shall be filed with the Environmental Sciences Section no later than 30 days after the end of the reporting period for which the report is made.

Test data shall be complete, accurate, include all supporting chemical/physical measurements and all concentration/response data, and be certified by laboratory supervisor and ORC or approved designate signature. Total residual chlorine of the effluent toxicity sample must be measured and reported if chlorine is employed for disinfection of the waste stream.

Should there be no discharge of flow from the facility during a month in which toxicity monitoring is required, the permittee will complete the information located at the top of the aquatic toxicity (AT) test form indicating the facility name, permit number, pipe number, county, and the month/year of the report with the notation of "No Flow" in the comment area of the form. The report shall be submitted to the Environmental Sciences Section at the address cited above.

Should the permittee fail to monitor during a month in which toxicity monitoring is required, monitoring will be required during the following month.

Should any test data from this monitoring requirement or tests performed by the North Carolina Division of Water Quality indicate potential impacts to the receiving stream, this permit may be re-opened and modified to include alternate monitoring requirements or limits.

NOTE: Failure to achieve test conditions as specified in the cited document, such as minimum control organism survival, minimum control organism reproduction, and appropriate environmental controls, shall constitute an invalid test and will require immediate follow-up testing to be completed no later than the last day of the month following the month of the initial monitoring.

A. (5) RE-OPENER CONDITION

This permit shall be modified, or revoked and reissued to incorporate additional toxicity limitations and monitoring requirements in the event toxicity testing or other studies conducted on the effluent or receiving stream indicate that detrimental effects may be expected in the receiving stream as a result of this discharge.

A. (6) BIOCIDES CONDITION

The permittee shall not use any biocide except those approved in conjunction with the permit application. The permittee shall notify the Director in writing not later than ninety (90) days prior to instituting use of any additional biocide used in cooling systems which may be toxic to aquatic life other than those previously reported to the Division of Water Quality. Such notification shall include completion of Biocide Worksheet Form 101 and a map locating the discharge point and receiving stream.

North Carolina Department of Environmental Quality

Pat McCrory
Governor

Donald R. van der Vaart
Secretary

October 28, 2015

Mr. Michael Johnson, PE
Environmental Manager
The Chemours Company FC, LLC
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

Subject: NPDES Permit Modification
Permit NC0003573
Ownership Change
Bladen County
Class II Facility

Dear Mr. Johnson:

Division personnel have reviewed and approved your request for permit modification of the subject permit, to reflect new facility ownership effective July 1, 2015. Accordingly, we are enclosing modified pages to reflect the new ownership. Please insert these modified pages into your current permit. A complete review of this permit will be conducted with your next permit renewal in 2016. This permit modification is issued pursuant to the requirements of North Carolina General Statute 143-215.1 and the Memorandum of Agreement between North Carolina and the U.S. Environmental Protection Agency dated October 15, 2007 (or as subsequently amended). If you have any questions, feel free to contact me at 919-807-6390 or via email at tom.belnick@ncdenr.gov.

Sincerely,



for S. Jay Zimmerman, P.G.
Director, Division of Water Resources

cc: NPDES Files
Central Files

Ecopy:
EPA Region 4
DWR Fayetteville Regional Office/Water Quality
DWR Aquatic Toxicology

1601 Mail Service Center, Raleigh, North Carolina 27699-1601
Phone: 919-707-8600 \ Internet: www.ncdenr.gov

**STATE OF NORTH CAROLINA
DEPARTMENT OF ENVIRONMENTAL QUALITY
DIVISION OF WATER RESOURCES**

NPDES PERMIT

**TO DISCHARGE WASTEWATER UNDER THE
NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM**

In compliance with the provisions of North Carolina General Statute 143-215.1, other lawful standards and regulations promulgated and adopted by the North Carolina Environmental Management Commission, and the Federal Water Pollution Control Act, as amended,

The Chemours Company FC, LLC

is hereby authorized to discharge wastewater and stormwater from a facility located at

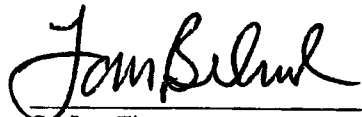
**Chemours Company- Fayetteville Works
22828 NC Highway 87 W
Fayetteville
Bladen County**

to receiving waters designated as the Cape Fear River in the Cape Fear River Basin in accordance with effluent limitations, monitoring requirements, and other conditions set forth in Parts I, II, III, and IV hereof.

The permit modification shall become effective July 1, 2015.

This permit and the authorization to discharge shall expire at midnight on October 31, 2016.

Signed this day October 28, 2015.



S. Jay Zimmerman, P.G.
Director, Division of Water Resources
By Authority of the Environmental Management Commission

SUPPLEMENT TO PERMIT COVER SHEET

All previous NPDES Permits issued to this facility, whether for operation or discharge are hereby revoked, and as of this issuance, any previously issued permit bearing this number is no longer effective. Therefore, the exclusive authority to operate and discharge from this facility arises under the permit conditions, requirements, terms, and provisions included herein.

The Chemours Company FC, LLC

is hereby authorized to:

1. Continue to operate existing wastewater treatment facilities consisting of:
 - equalization;
 - neutralization;
 - aerated pre-digester tank;
 - nutrient feed system;
 - aeration tank;
 - three clarifiers;
 - effluent flow measurement;
 - DAF unit;
 - rotary filter for sludge thickening;
 - sludge pump;
 - sludge filter press; and
 - steam heated sludge dryers.
2. Discharge treated process wastewater from Butacite®, Nafion®, SentryGlas®, and PVF (polyvinyl fluoride resin), process stormwater, sanitary wastewater, and co-neutralized regenerate from said treated facilities through internal outfall 001;
3. Discharge stormwater, non-contact cooling water, boiler blowdown and condensate, cooling tower blowdown, and treated wastewater effluent from 001, through outfall 002 at the location specified on the attached map into the Cape Fear River, a class C, WS-IV water in the Cape Fear River Basin.



Linda Miles <milesfirm@gmail.com>

Fwd: Npdes permitted

1 message

Beth Eckert <Beth.Eckert@cfpua.org>

Thu, Jun 8, 2017 at 1:35 PM

To: Linda Miles Firm <milesfirm@gmail.com>, GHOUSE <GHOUSE@brookspierce.com>

Beth Eckert

Begin forwarded message:

From: "Gregson, Jim" <jim.gregson@ncdenr.gov>

Date: April 27, 2017 at 11:09:48 AM EDT

To: Beth Eckert <Beth.Eckert@cfpua.org>

Subject: RE: Npdes permitted

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section
Division of Water Resources
Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
Jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405

Email correspondence to and from this address is subject to the
North Carolina Public Records Law and may be disclosed to third parties.

-----Original Message-----

From: Beth Eckert [mailto: Beth.Eckert@cfpua.org]

Sent: Wednesday, April 26, 2017 8:24 AM

To: Gregson, Jim <jim.gregson@ncdenr.gov>

Subject: Npdes permitted

Hey Jim

There is a manufacturing plant, Chemora, that discharges via NPDES permit into the cape fear river between here and Fayetteville. Is this group in your area and if so can I get a copy of there permit?

Beth Eckert

8 attachments

 **NC0003573 Ownership Change.pdf**
214K

 **ATT00001.htm**
1K

 **Ownership Change 2015.docx**
35K

 **ATT00002.htm**
1K

 **Cover Ltr 2015.docx**
30K

 **ATT00003.htm**
1K

 **3573-fact sheet-2011.pdf**
206K

 **ATT00004.htm**
1K

1) Is our drinking water safe?

Since the State of North Carolina and EPA establish the drinking water standards we follow, we will be looking to them to determine whether this currently unregulated contaminant should be regulated at the point of discharge to the Cape Fear River. In the meantime, CFPUA continues to meet all state and federal standards for water safety.

2) What do we know about GenX?

We know that it is unregulated and measured in the parts per trillion, but there is little information regarding its health effects on humans. As the compound is a by-product of Chemours' manufacturing processes, they are perhaps better suited to answer questions about the nature of GenX.

3) What can be done at the treatment plant to remove GenX from the water?

GenX is an emerging contaminant, and we are unaware of technologies capable of removing this compound from the water. Thus, the more important question is: what can we do to remove this compound from the river?

4) With GenX in the Cape Fear River, what can/will CFPUA do to ensure the water is safe?

CFPUA treats its source water above and beyond current state and federal standards, and maintains a robust sampling and monitoring schedule. Additionally, we believe in the importance of participating in studies such as this one to ensure that emerging contaminants are discovered and regulated. CFPUA believes the best next step is to determine if this compound needs to be regulated and, if so, ensure that enforcement methods keep it from entering the Cape Fear River.

5) Does CFPUA monitor for GenX? If not, why?

Due to GenX's status as an emerging and unregulated contaminant, there are no certified methods to monitor and test for the substance. It is our understanding that Chemours is not permitted to discharge this compound into the river, and we were not informed that it was in the river. For more information on permitting and compliance enforcement, please contact the State of North Carolina—the agency responsible for monitoring and regulating dischargers on the River.

6) If CFPUA participated in the study and knew the results, why did you not release them earlier?

After becoming aware of the study's findings, CFPUA staff initiated, and maintained, conversations with the researchers associated with the study to learn more about the compound and the available testing options. Additionally, CFPUA contacted the State of North Carolina, the agency responsible for regulating Chemours' discharge into the Cape Fear River, to inform them of the findings.

7) Can customers put a filter on their tap to remove GenX?

GenX is a new, unregulated compound and we are unaware of technologies capable of removing it from the water. There are no commercial laboratories capable of testing for the compound, which makes it difficult to know whether methods such as boiling or filtering can remove it.

8) Are you notifying customers about GenX?

Information about GenX is limited, as it is a proprietary compound of Dupont and Chemours permitted by the State of North Carolina. We hope that the company and the State of North Carolina will provide more information in the future.



**Evaluation of substances used in the GenX
technology by Chemours, Dordrecht**

RIVM Letter report 2016-0174
M. Beekman et al.

Publiekssamenvatting

Beoordeling van de stoffen die door Chemours (Dordrecht) bij de GenX technologie worden gebruikt

Sinds 2012 gebruikt fabrikant Chemours (Dordrecht) de GenX-technologie om plastics (fluorpolymeren) te maken. Bij deze technologie zijn de omstreden PFOA-verbindingen vervangen door de stoffen FRD-902 en FRD-903 en E1. Naar verwachting vormt de uitstoot van deze stoffen door de fabriek via de lucht geen risico voor de gezondheid van omwonenden.

Dit blijkt uit onderzoek van het RIVM. In opdracht van het ministerie van Infrastructuur en Milieu (IenM) is onderzocht in hoeverre de drie stoffen schadelijk zijn voor omwonenden van de fabriek. Hiervoor is in de wetenschappelijke literatuur en de informatie in de Europese stoffenwetgeving REACH onderzocht wat bekend is over de eigenschappen van de genoemde stoffen. Daarnaast is op basis van zowel de maximaal vergunde hoeveelheid als de emissiegegevens die Chemours heeft verstrekt, berekend in welke mate ze zijn vrijgekomen.

FRD-903 wordt gebruikt om FRD-902 te maken. E1 ontstaat tijdens het productieproces. FRD-903 en E1 worden via de fabrieksschoorsteen naar de lucht uitgestoten. Net als PFOA zijn geperfluorideerde koolwaterstoffen FRD-902 en FRD-903 en E1 slecht afbreekbaar in het milieu. Ook veroorzaken FRD-903 en FRD-902 vergelijkbare schadelijke effecten als PFOA (zoals kankerverwekkend en effecten op de lever). Deze stoffen zijn wel minder schadelijk voor de voortplanting dan PFOA; bij PFOA is dit aspect juist de reden om deze stof als zeer zorgwekkend te beschouwen. In tegenstelling tot PFOA lijken FRD-903 en FRD-902 zich niet in de mens op te hopen.

Voor FRD-903 en FRD-902 heeft het RIVM een veilige grenswaarde voor de algemene bevolking afgeleid op basis van een worst-case scenario. De concentratie FRD-903 in lucht blijft onder deze grenswaarde. Voor E1 ontbreekt informatie om een grenswaarde te kunnen bepalen. Op basis van de beperkt beschikbare informatie wordt verondersteld dat deze stof waarschijnlijk minder schadelijk is dan PFOA.

Kernwoorden: GenX, PFOA alternatief, PBT beoordeling, risicobeoordeling, REACH

MH
M. H. M. H.

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Samenvatting

In dit rapport worden de perfluorverbindingen (FRD-903, FRD-902 en E1) geëvalueerd. Deze verbindingen worden gebruikt of ontstaan bij de GenX technologie voor het maken van fluoropolymeren bij Chemours in Dordrecht. Bij deze technologie wordt geen gebruik gemaakt van de omstreden PFOA-verbindingen die eerder werden toegepast. Hierbij worden de volgende vragen beantwoord:

1. Wat is bekend over de PBT¹ eigenschappen van FRD-903, FRD-902 en E1?
2. Wat is bekend over de eventuele CMR² en STOT RE³ eigenschappen (met name lever- en niertoxiciteit) van FRD-903, FRD-902 en E1?
3. Wat is bekend over de emissie van FRD-903 en E1 bij Chemours in Dordrecht?
4. Wat is er te zeggen over de gezondheidseffecten (nu en in de toekomst) voor de omwonenden als gevolg van blootstelling aan FRD-903 en E1?

Aangezien alle beschikbare toxiciteitsstudies zijn uitgevoerd met het ammoniumzout (FRD-902) en niet met het zuur (FRD-903), is de beoordeling van FRD-903 in dit rapport gebaseerd op de gegevens van FRD-902. Het is gerechtvaardigd om de gegevens van FRD-902 te gebruiken voor FRD-903 omdat de effecten in het lichaam bij beide stoffen veroorzaakt worden door het anion (2,3,3,-tetrafluoro-2-(heptafluoropropoxy)propanoate).

Bij de eerste vraag concludeert het RIVM dat het niet is uitgesloten dat de aan de GenX technologie gerelateerde stoffen (FRD-903, FRD-902 en E1) voldoen aan de PBT of vPvB⁴ criteria. Alle drie de stoffen zijn perfluorverbindingen en hiervan kan worden gesteld dat ze vrijwel zeker zeer slecht in het milieu worden afgebroken. Aangezien FRD-903 en FRD-902 sneller dan PFOA het lichaam verlaten, wordt verwacht dat beide stoffen een geringere bioaccumulatie vertonen. Er kan echter geen definitieve conclusie worden getrokken omdat data over de eliminatiesnelheid bij de mens ontbreken. Voor de stof E1 is er onvoldoende informatie om een conclusie te trekken over de mogelijke bioaccumulatie. Aangezien E1 geen hydrofiele groep bevat, is de verwachting dat de eliminatie van E1 trager is en daarmee een hogere potentie voor bioaccumulatie heeft dan PFOA. Aan de andere kant wordt E1 waarschijnlijk weer gemakkelijk uitgeademd. FRD-903 en FRD-902 zijn naar verwachting minder gevaarlijk dan PFOA, maar ook hiervoor kunnen geen definitieve conclusies ten aanzien van het T criterium worden getrokken. E1 voldoet waarschijnlijk niet aan het T criterium van de PBT analyse.

¹ Persistent, Bioaccumulative and Toxic

² Carcinogenic, mutagenic or toxic for the reproduction

³ Specific target organ toxicity after repeated exposure

⁴ Very Persistent and very Bioaccumulative

Bij de beoordeling van de CMR en STOT RE eigenschappen, wordt geconcludeerd dat FRD-903 en FRD-902 geclassificeerd zouden moeten worden als kankerverwekkend categorie 2 (mogelijk kankerverwekkend voor de mens). Verder laten de beschikbare studies zien dat beide stoffen niet mutageen zijn. De beperkte reproductie-toxische effecten die gevonden worden, leiden normaal gesproken niet tot een classificatie op dit onderdeel. Dit is in tegenstelling tot PFOA, welke geclassificeerd is als schadelijk voor de voortplanting (categorie 1B). Ten slotte is het lastig om de toxiciteit voor organen (zoals lever en nier) te beoordelen omdat de testen die bij muizen zijn gedaan, zijn uitgevoerd bij doseringen lager dan de voorgeschreven doseringen in de guidance documenten. Dit kan een indicatie zijn dat classificatie als STOT RE categorie 2 noodzakelijk is. De effecten die bij de rat zijn waargenomen, zijn marginaal en eveneens moeilijk te beoordelen vanwege de grote stappen in de doseringsniveaus die zijn gehanteerd. De effecten op de lever zijn bij FRD-902 en PFOA waargenomen bij ongeveer vergelijkbare doseringen.

De beschikbare informatie over de toxiciteit van E1 is beperkt, maar de informatie die beschikbaar is, wijst op een lage tot zeer lage toxiciteit. Deze conclusie wordt ondersteund door informatie over de toxiciteit van vergelijkbare verbindingen. Wel dient opgemerkt te worden dat alle beschikbare studies enkel zijn uitgevoerd met mannetjes proefdieren en slechts van beperkte blootstellingsduur waren. De beschikbare in vitro en in vivo mutageniteitsdata, gecombineerd met de data van vergelijkbare verbindingen, tonen aan dat het onwaarschijnlijk is dat E1 mutageen is. Verder laten de beschikbare gegevens zien dat het waarschijnlijk niet nodig is om E1 te classificeren voor acute toxiciteit en voor STOT RE door inademing. De beoordeling van E1 voor classificatie op andere eindpunten, waaronder carcinogeniteit, reproductietoxiciteit en STOT RE door orale blootstelling, is niet mogelijk op basis van de nu beschikbare informatie.

Voor FRD-903 en FRD-902 wordt in dit rapport – rekening houdend met een worst-case aanpak – een chronische inhalatieblootstellingslimiet van 73 ng/m^3 afgeleid. Hierbij is een extra veiligheidsmarge gehanteerd vanwege de onzekerheid over de mogelijke bioaccumulatie van deze stoffen. De jaargemiddelde concentraties van FRD-903 in de lucht zijn berekend op basis van de maximaal vergunde hoeveelheden. Deze berekening laat zien dat de concentratie FRD-903 in lucht 20 ng/m^3 is bij de dichtstbijzijnde bewoonde gebieden (de dijk aan de overkant van de rivier) en lagere concentraties verder van de fabriek. De berekening op basis van de gerapporteerde emissies in 2014, komt uit op 15 ng/m^3 voor de dichtstbijzijnde bewoonde gebieden. Het vergelijken van deze berekende concentraties met de afgeleide grenswaarde van 73 ng/m^3 leidt tot de conclusie dat op basis van de beschikbare informatie er geen gezondheidsrisico voor de omwonenden van de Chemours fabriek door blootstelling aan FRD-903 te verwachten is.

De informatie over de toxiciteit van E1 is beperkt. De gegevens over de toxiciteit van E1 zijn onvoldoende om een inhalatieblootstellingslimiet voor E1 af te leiden. De jaargemiddelde concentraties van E1 in de lucht zijn berekend op basis van de maximaal vergunde hoeveelheden. Deze berekening laat zien dat de concentratie E1 in lucht 40 ng/m^3 is bij de

dichtstbijzijnde bewoonde gebieden (de dijk aan de overkant van de rivier) en lagere concentraties verder van de fabriek. De berekening op basis van de gerapporteerde emissies in 2014 komt uit op 20 ng/m³ voor de dichtstbijzijnde bewoonde gebieden. Vanwege de ontbrekende informatie over de toxiciteit van E1, kan er geen conclusie worden getrokken over een mogelijk gezondheidsrisico voor de omwonenden van de Chemours fabriek door blootstelling aan E1.

Summary

In this report, the GenX related perfluorinated substances (FRD-903, FRD-902 and E1) are evaluated. These substances are used or are formed during the production of fluoropolymers by Chemours (Dordrecht) applying the GenX technology. In this technology, the controversial PFOA substances are replaced. The following questions are addressed in the evaluation:

1. What is known about the PBT⁵-properties of FRD-903, FRD-902 and E1?
2. What is known about the possible CMR⁶-properties and STOT RE-properties⁷ (especially the toxicity to kidney and liver) of FRD-903, FRD-902 and E1?
3. What is known about the emission of FRD-903 and E1 by Chemours (Dordrecht)?
4. What are the possible health effects (now and in the future) for people living in the vicinity of the Chemours Dordrecht plant due to exposure to FRD-903 and E1?

For FRD-903 the evaluation is based on read across from FRD-902, since all available toxicological studies were performed with the ammonium salt (FRD-902). Read-across of the toxicological properties of the ammonium salt to the acid (FRD-903) is considered justified for systemic effects as after dissolution and dissociation of the acid and the salt the absorption in the intestinal tract and the lungs and distribution over the body of the anion (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate) will be the same.

As to the first question above, it is concluded that RIVM cannot exclude that the GenX related substances meet the PBT/vPvB⁸ criteria. All evaluated substances (FRD-903, FRD-902 and E1) are perfluorinated compounds and can be regarded as certainly very persistent. Since FRD-903 and FRD-902 are more rapidly eliminated than PFOA, it is expected that both substances bioaccumulate to a lesser degree than PFOA does. However, it is not possible to reach a conclusion on the human bioaccumulation potential in absence of data on the human clearance time. For the substance E1, insufficient information is available to draw a conclusion about the bioaccumulation potential. Since E1 contains no hydrophilic group, the human clearance time of the substance and the bioaccumulation potential are expected to be higher than for PFOA, although E1 has the potential to be excreted via exhalation. FRD-903 and FRD-902 are considered less hazardous compared to PFOA. However, no definitive conclusion can be reached whether they meet the T criteria. E1 will most likely not meet the T criteria.

For the CMR and STOT RE properties, it is concluded that classification as carcinogenic category 2 (suspected human carcinogen) is justified for

⁵ Persistent, Bioaccumulative and Toxic

⁶ Carcinogenic, mutagenic or toxic for the reproduction

⁷ Specific Target Organ Toxicity, Repeated Exposure

⁸ Very Persistent and very Bioaccumulative

FRD-903 and FRD-902. The available studies show that both substances are not mutagenic. On reproductive toxicity the limited effects observed in presence of maternal toxicity do not normally result in classification, whereas PFOA is classified as toxic for the reproduction (category 1B). The requirement of STOT RE 2 (like liver and kidney) is difficult to assess due to dose levels tested in mice clearly below the guidance values, which may be taken as an indication that STOT RE 2 is needed. The effects in the rat are borderline and difficult to assess due to the large steps in the dose levels. Effects on the liver are observed at the similar dose levels for FRD-902 and PFOA.

The available information on the toxicity of E1 is limited but that information indicates that E1 has a low to very low toxicity. This is supported by the repeated dose toxicity information on some structural analogues. However, all available studies were performed in male animals only and were of limited duration only. The available in vitro and in vivo data on mutagenicity combined with the read-across data show that E1 is unlikely to be mutagenic. In addition, the available data indicate no requirement for classification for acute toxicity nor probably for STOT RE via inhalation. The requirement for classification for other hazard classes including carcinogenicity, reproductive toxicity and STOT RE via oral exposure, however, is unknown.

A chronic inhalation exposure limit of 73 ng/m^3 for FRD-903 and FRD-902 is derived in the present report in a worst-case approach, taking into account an extra safety margin due to uncertainty in the accumulation potential. The year-average air concentrations of FRD-903 were calculated based on the permitted emissions. This led to estimated concentrations in air of about 20 ng/m^3 for the nearest populated areas (along the dike opposite side of the river) and lower concentrations at greater distances from the plant. Based on the recorded emissions for 2014 the estimated concentrations for the nearest populated areas are about 15 ng/m^3 . Comparing these concentrations with the limit value of 73 ng/m^3 leads to the conclusion that based on the available data, no health risk is expected for people living in the vicinity of the Chemours Dordrecht plant due to exposure to FRD-903.

The information on the toxicity of E1 is limited. The data are insufficient for deriving an inhalation exposure limit for the general population. The year-average air concentrations for E1 were calculated based on the permitted emissions. This led to estimated concentrations in air of about 40 ng/m^3 for the nearest populated areas (along the dike at the opposite side of the river) and lower concentrations at greater distances from the plant. Based on recorded emissions for 2014 the estimated concentrations for the nearest populated areas are about 20 ng/m^3 . Due to the insufficient health effects information available for E1, these concentrations cannot be evaluated as to the possible health risk they might pose for people living in the vicinity of the Chemours plant in Dordrecht.

1

Introduction

DuPont has developed the GenX technology as a polymerization aid to make fluoropolymers like teflon without the use of perfluorooctanoic acid (PFOA)⁹. PFOA is an important representative of the substance group of per- and polyfluorinated substances (PFASs). PFASs consist of carbon chains of different chain length, where the hydrogen atoms are completely (perfluorinated) or partly (polyfluorinated) substituted by fluorine atoms. The very stable bond between carbon and fluorine is only breakable with high energy input. Therefore, perfluorinated acids, like PFOA, are not degradable in the environment. The hazard profile of PFOA is well known: PFOA is a persistent, bioaccumulative, and toxic substance (PBT), which may cause severe and irreversible adverse effects on the environment and human health. Due to its PBT properties and toxicity to the reproduction, PFOA and its ammonium salt (APFO) have been identified as substances of very high concern (SVHC) under REACH¹⁰. Further, a proposal for restricting the manufacture and use of PFOA is under discussion within the context of the REACH regulation¹¹.

Chemours Dordrecht has started to replace the use of PFOA by the GenX technology from 2005 (in the USA) onwards and has completely ceased the use of PFOA since 2012 at the plant in Dordrecht. This technology is also based on perfluorinated substances. According to the manufacturer, the resin manufacturing process includes the thermal transformation of the GenX processing aid (FRD-902) into the hydrophobic water-insoluble hydride (E1). The present assessment focuses on the GenX related substances:

- the precursor 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoic acid (FRD-903),
- the processing agent ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate (FRD-902) and
- the transformation product heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether (E1).

Another substance, perfluorisobutene, a by-product emitted during the production of fluoropolymers is cause for concern due to its highly toxic properties. This substance is not covered by the current assessment because this substance is not specific to the GenX technology. This assessment compares the specific substances used in the GenX technology with APFO.

Concerns have been raised about the hazard and risk properties of the GenX technology used by Chemours (Dordrecht) and therefore the Ministry of Infrastructure and Environment has requested RIVM to

⁹ <https://www.chemours.com/Dordrecht-Plant/nl/assets/downloads/pdf/2016-0909-met-behulp-van-genx-fact-sheet.pdf>

¹⁰ Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

¹¹ Annex XV restriction dossier, <https://echa.europa.eu/previous-consultations-on-restriction-proposals/-/substance-rev/1908/term>.

evaluate the substances used in this GenX technology. More specifically the Ministry asks RIVM to answer the following questions:

1. What is known about the PBT-properties of FRD-903 and E1¹²?
2. What is known about the possible CMR-properties and STOT RE-properties (especially the toxicity to kidney and liver) of FRD-903 and E1?
3. What is known about the emission of FRD-903 and E1 by Chemours (Dordrecht)?
4. What are the possible health effects (now and in the future) for people living in the vicinity of the Chemours Dordrecht plant due to exposure to FRD-903 and E1?

The assessment by RIVM is based on available literature, which mainly originates from REACH. For FRD-902 one REACH registration dossier is available (10-100 tonnes per year). FRD-902 is on the REACH Community Rolling Action Plan (CoRAP) for 2017 (for substance evaluation on the potential PBT/vPvB properties, which will be conducted by Germany). The acid and the hydride are not registered. There is no harmonised classification available for any of the substances. FRD-902 is described in the REACH Annex XV restriction dossier of PFOA under the chapter on alternatives. The comparison made between PFOA and FRD-902 in this restriction dossier is used for the present assessment and is supplemented with data from the registration dossier, studies provided by Chemours and publications in the scientific literature.

No additional information was retrieved on the human toxicological and environmental properties of FRD-903. Therefore, assessment of these properties in chapter 3 and 4 is based on read-across with the ammonium-salt (FRD-902). For E1 available data proved to be limited only and for this chemical the current assessment is therefore limited to a screening and is mainly based on QSAR estimations and mainly old data provided by Chemours.

It has to be noted that in accordance to the request from the Ministry, the possible health effects for people living near the Chemours plant is assessed. Exposure to these substances by inhalation is considered the most relevant route for people living near the Chemours plant. Further information is needed to assess the possibility of exposure by contaminated drinking water.

Report structure

Some general information on the substances used in the GenX technology is given in chapter 2. In chapter 3 and 4 of this report the PBT and human health (CMR, STOT-RE) properties, respectively, are evaluated. In chapter 4, exposure limits for the general population are derived for both FRD-903 and E1. Chapter 5 presents the known emissions of the substances by Chemours. In chapter 6 the possible health effects are described. And finally, concluding remarks are made in chapter 7.

¹² Including possible other relevant substances related to the GenX technology.

2 General information

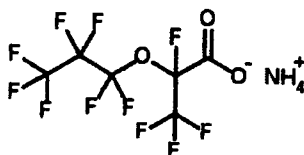
2.1 Description GenX technology

FRD-902 is used as processing aid in the Teflon PTFE and Teflon FEP plants of Chemours. Other uses of FRD-902 are not described in the registration dossier or in the literature. FRD-902 is manufactured by mixing FRD-903 with an ammonium hydroxide solution. FRD-903 is imported.

FRD-902 controls the polymerization to make fluoropolymers. Fluoropolymer resins and finished goods are used in many applications like wire cables and Teflon coating. During the resin manufacturing process, FRD-902 is transformed into the hydrophobic water-insoluble hydride (E1). During the process, FRD-903 and E1 are emitted to air from the Teflon PTFE and from the Teflon FEP plants. Furthermore, FRD-902 and FRD-903 are emitted to wastewater. After removal of these compounds, the wastewater is sent to the local municipal sewage treatment plant. Exposure of people living in the vicinity of the Chemours is expected to be primarily through the emission to air.

2.2 Substance identity and status of FRD-902

Name: ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate
 CAS-number: 62037-80-3
 EC-number: 700-242-3
 Synonyms: FRD-902, C3-dimer salt
 IUPAC name: ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate
 Structure: C₆H₄NF₁₁O₃



REACH: registered by Chemours Netherlands BV: 10 - 100 TPA, full registration
 CLP¹³: no harmonised classification, 28 notifiers to the CLP inventory (19 September 2016) (Acute Tox. 4; H302, Eye Dam. 1; H318, STOT RE 2; H373 (blood)), see table 1.

¹³ Regulation (EC) No 1272/2008 on the classification, labelling and packaging of substances and mixtures (CLP Regulation)

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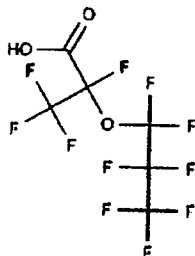
Physical chemical properties¹⁴

Melting point: 208 °C (99.4% purity)
 Freezing point: -21 °C (86% purity)
 Vapour pressure: 0.012 Pa (99.4% purity)
 Solubility in water: >1000 g/L (99.4 % purity)
 Form: liquid (86% purity, marketed form), solid (dried substance, 99.4% purity)
 Color: colourless liquid
 Density: 1118 g/L (99.4% purity)
 Dissociation constant: pKa: 3.82 (86% purity)

2.3

Substance identity and status of FRD-903

Name: 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid
 CAS-number: 13252-13-6
 EC-number: 236-236-8
 Synonyms: FRD-903, C3-dimer
 IUPAC name: 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid, perfluoro-2-methyl-3-oxahexanoic acid
 Structure: C₆HF₁₁O₃



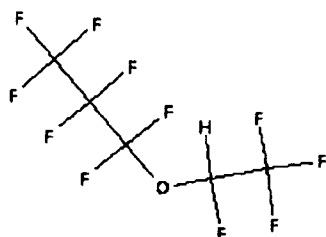
REACH: not registered
 CLP: no harmonised classification, 99 notifiers to the CLP inventory (including Acute Tox. 4; H302, Skin Corr. 1B or 1C; H314, Eye Dam. 1; H318, STOT SE 3; H335 (Respiratory) and no classification), see table 2.

¹⁴ REACH registration data, 19 September 2016

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2.4 Substance identity and status of E1

Name: heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether
 CAS-number: 3330-15-2
 EC-number: 671-353-1
 Synonyms: propane, 1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)- E1
 IUPAC name: heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether
 Structure: C₅H₂F₁₀O



REACH: not registered
 CLP: no harmonised classification, 3 notifiers to the CLP inventory (29 August 2016)

Table 3. Notifications to the CLP inventory for E1 (19 September 2016).

Skin Irrit. 2	H315	H315	GHS07 Wng	GHS07 Wng	State/Form IUPAC Names	2
	H319	H319				
STOT SE 3	H335 (Lungs) (Inhalation)	H335	GHS07 Wng	GHS07 Wng	1	
Skin Irrit. 2	H315	H315				
Eye Irrit. 2	H319	H319	GHS07 Wng	GHS07 Wng	1	
STOT SE 3	H335 (Not Specified)	H335				

Physical chemical properties (MSDS, 2007)

Vapour pressure: 30 kPa
Solubility in Water: 7 mg/L
Henry's law constant: $5.54 \times 10^2 \text{ Pa}\cdot\text{m}^3/\text{mol}$ (calculated)
Odor: no Distinct Odor

Form: liquid
Color: clear, colorless
Density: 1.54 g/mL
Relative density: 1.59
Viscosity: 0.5 cp
Pour point: -155 °C (-247 F)
Log10Pow: 3.83 ± 0.04
Freezing point: -54.9°C
Boiling point: 49°C (measurement 1) 40.6°C (measurement 2)

3 PBT properties

In this chapter a PBT/vPvB assessment according to the criteria for the identification of PBT substances and vPvB substances in Annex XIII of the REACH regulation is made¹⁵.

3.1 Persistence FRD-902

FRD-902 is hydrolytically stable, has surface-active properties and is not readily biodegradable. In the ready biodegradation test (OECD 301B16) 0% degradation was observed after 28 days. In addition, in an inherent biodegradation test (OECD 302C) no biodegradation was observed after 28 days. Simulation tests (which are performed to establish half-life values) have not been conducted for FRD-902. As a result, no definitive conclusion on the P and vP criteria can be drawn. However, as FRD-902 is a perfluorinated ether-compound, it is almost certain that FRD-902 will be P and vP. This is strongly supported by all QSAR predictions (especially the Biowin QSAR models).

Given the log K_{oc} values of respectively 1.1 and 1.08, the low Henry's law constant of $4.06E-06$ Pa·m³/mol and a water solubility of 207 mg/L, FRD-902 is expected to have low potential to bind to sludge and soil. On the other hand, surface-active properties tend to increase the binding potential. In water FRD-902 will be dissociated at ambient temperature at neutral pH (pKa=3.82; pKb=8.10; OECD 112 at 20°C).

3.2 Bioaccumulation FRD-902

As the evaluation of PFOA pointed out, accumulation in fat tissue is not relevant for assessing the bioaccumulation potential of perfluorinated compounds. Perfluorinated compounds bind to proteins, in particular in blood and liver. The log K_{ow} is only indicative of binding to lipids, not for binding to proteins and does not provide an indication on bioaccumulation potential of perfluorinated compounds. To illustrate, the log K_{ow} of PFOA (2.69) is far below the screening criterion for bioaccumulation. Still, elevated levels of PFOA in human blood and excretion via breastmilk are observed widely. In addition, biomagnification factors in the terrestrial food chain exceed the value of 1. Although such data are not available for FRD-902, based on the perfluorination and analogy with PFOA, it is expected that FRD-902 will bioaccumulate via protein binding.

It is unclear which substance properties determine the protein binding potential, but possibly the number of perfluorinated carbon atoms is crucial for protein binding. FRD-902 has 4.5 perfluorinated carbon atoms (one carbon atom contains a carboxyl group and is therefore not completely perfluorinated), whereas PFOA (which is concluded to be bioaccumulative (B)) has seven perfluorinated carbon atoms. Another

¹⁵ <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=L:2011:069:0007:0012:EN:PDF>

¹⁶ OECD guideline, see <http://www.oecd.org/chemicalsafety/testing/oecdguidelinesforthetestingofchemicals.htm>

perfluorinated compound, PFHxA (which is concluded to be not B) has five perfluorinated carbon atoms, but does not contain ether bonds. Within this comparison, the effect of the ether bond on the protein-binding potential is unknown.

A bioconcentration test with the acid FRD-903 shows limited bioconcentration in carps (<30; Hoke et al., 2016), which is expected given the high water solubility and is in agreement with PFOA.

Oral toxic kinetic studies (Gannon et al., 2016) with mice and rats indicate that FRD-902 is easily absorbed and fully excreted via the urine without metabolism within hours up to seven days. The clearance time of FRD-902 in mice, rats and monkeys is an order of a magnitude lower compared to PFOA.

In view of this, FRD-902 may be expected to bioaccumulate to a lesser extent compared to PFOA. However, the human clearance time for PFOA is an order of magnitude higher (2-4 yrs.) in comparison to all tested animal species (up to 60 days). It is not possible to draw a conclusion on the bioaccumulation potential of FRD-902 in absence of data on the human clearance time.

3.3

Toxicity FRD-902

As indicated 2.2, there is no harmonized classification available for this substance. The self-classification notifications are: Acute Tox. 4, Eye Dam. 1 and STOT RE 2 (substances presumed to have the potential to be harmful to human health following repeated exposure).

In paragraphs 4.1 and 4.2 an assessment of the human health toxicity is given. It is concluded that for FRD-902 it is difficult to assess the requirement for STOT RE 2. Furthermore, it is concluded that FRD-902 will normally not result in classification for mutagenicity and toxic for the reproduction. For carcinogenicity, classification as category 2 is justified.

For aquatic organisms, this substance is not acutely toxic (LC/EC50 > 100 mg/L) or chronically toxic (NOEC > 1 mg/L; lowest NOEC 1.08 mg/L). Therefore, for ecotoxicity, this substance does not meet the T criterion (a factor 100 above the criteria).

Given the available toxicity data it can be concluded that FRD-902 is less toxic compared to PFOA. No conclusion can be drawn whether the effects observed after repeated exposure are sufficient proof of chronic toxicity to meet the T-criterion. Based on the data used for this report, the substance should be considered borderline T.

3.4

Conclusion on PBT/vPvB status for FRD-902

- P/vP: Since FRD-902 is a perfluorinated compound, the substance is almost certain P/vP. All data and QSAR model predictions point in this direction.
- B: FRD-902 is more rapidly eliminated than PFOA. Consequently, FRD-902 is expected to bioaccumulate less than PFOA. However, it is not possible to reach a conclusion on the human bioaccumulation potential of FRD-902 in absence of data on the human clearance time.

- T: FRD-902 is less toxic compared to PFOA; however, no definitive conclusion on the T criteria can be reached since the substance is considered borderline T for STOT RE.

Overall, it cannot be excluded that FRD-902 meets the PBT/vPvB criteria.

3.5 Persistence, bioaccumulation and toxicity FRD-903

No additional information was retrieved on the human toxicological and environmental properties of FRD-903. Therefore, no separate PBT/vPvB assessment for FRD-903 is made, the conclusions on FRD-902 are valid for FRD-903 as well.

The self-classification notifications for the acid are also comparable to FRD-902 (Acute Tox. 4, Skin Corr. 1C/1B, Eye Dam. 1 and STOT SE 3).

3.6 Persistence E1

E1 is potentially persistent based on the biodegradation QSARs Biowin2&3 (0.00 en 1.11) and Biowin6&3 (0.00 en 1.11). In addition, the PB score tool, as developed by the RIVM, characterizes E1 as persistent. Due to the perfluorination, it is almost certain that E1 is persistent and meets the P and vP-criteria.

3.7 Bioaccumulation E1

E1 does not dissociate; estimated log K_{ow} values are 3.44 (KOWWIN v1.68) and 4.25 (Biolum). The available bioaccumulation QSARs are based on lipid-binding accumulation and are not suitable for perfluoro compounds (such as E1), which are expected to accumulate via protein binding (like PFOA). In comparison to PFOA and FRD-902, it is expected that E1 has a higher bioaccumulation potential as it does not contain any hydrophilic groups (presumably resulting in a lower water solubility and slower excretion rate). However, the high vapour pressure may indicate that the substance is excreted via exhalation.

3.8 Toxicity E1

The information on classification and labeling of E1 (no harmonized classification and the following self-classification notifications: Skin Irrit 2, Eye irrit 2 and STOT SE 3) gives no indication that E1 potentially meets the T criteria for human toxicity. In paragraph 4.5 it is concluded that although the available information on E1 is limited, it indicates that E1 has a low to very low human toxicity. No information on ecotoxicity is provided in the MSDS (2007).

The ecotoxicity QSAR ECOSAR estimates a chronic toxicity NOEC for E1 of 0.68 mg/L for daphnids. Based on this estimate, E1 does not meet the T criteria for ecotoxicity.

3.9 Conclusion on PBT/vPvB status for E1

- P/vP: Since E1 is a perfluorinated compound, the substance is almost certain P/vP. All QSAR model predictions point in this direction.
- B/vB: Insufficient information is available to draw a conclusion

about the bioaccumulation potential of E1. Since E1 contains no hydrophilic group, the human clearance time of the substance and the bioaccumulation potential are expected to be higher than for PFOA (which meets the criteria for bioaccumulation), although E1 has the potential to be excreted via exhalation.

- T: E1 will most likely not meet the T criteria.

It cannot be excluded that E1 meets the vPvB criteria.

4 Human health properties

The toxicological information as used in the present evaluation is mainly based on the data as summarised by the registrant within the REACH registration dossier. In addition, Chemours provided some of the study reports on request of the RIVM. Further, two publications are available on kinetics and chronic toxicity and carcinogenicity, respectively, reporting studies also present in the registration dossier. Detailed summaries of the individual studies are provided in Annex I.

4.1 Human health hazards FRD-902

FRD-902 is classified as follows by the registrant:

- Acute Tox. 4 H302: Harmful if swallowed
- Eye Damage 1 H318: Causes serious eye damage
- STOT RE 2 H373: May cause damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>. Affected organs: Liver, Blood

Based on the data available in the registration dossier, the RIVM agrees with the classification as Acute Tox. 4; H302 and Eye Damage 1; H318. The classification with STOT RE 2 is based on the liver and red blood cell effects, as indicated by the affected organs in the available repeated dose toxicity studies. In table 4, a comparison is made of the effects at or around the guidance values for STOT RE 2 for the respective study duration with the effects which may support classification. Classification for STOT RE is based on a defined level of adverse effects occurring below specified dose levels depending on the study duration.

Table 4. Comparison of the effects at or around the guidance values for STOT RE 2.

Study	STOT RE 2 guidance value	Effects observed (dose in mg/kg bw/day)	RIVM remark	Reference ¹⁷
Oral, 28-day rat Males: 0.3, 3 and 30 mg/kg bw/day Females: 3, 30 and 300 mg/kg bw/day	300 mg/kg bw/day	30 mg/kg bw/day males/300 mg/kg bw/day females: increased liver beta-oxidation activity, increased liver and kidney weights, minimal hepatocellular hypertrophy, changes in serum lipids and proteins, and minimal decreases in red cell mass parameters (<7.9%)	Effects which may require classification (almost no information on effect size) as STOT RE including single cell necrosis and changes in serum lipids and proteins were observed at dose levels clearly below (males) or at (females) the guidance value for STOT RE 2.	Exp supporting repeated dose toxicity: oral.001

¹⁷ This table refers to the literature references as included in the REACH registration dossier. According to REACH, the reference details are considered confidential.

Study	STOT RE 2 guidance value	Effects observed (dose in mg/kg bw/day)	RIVM remark	Reference
Oral, 90-day rat Males: 0.1, 10 and 100 mg/kg bw/day and females 10, 100 and 1000 mg/kg bw/day	100 mg/kg bw/day	100 mg/kg bw/day (males): red cell mass reduction (11-13%), decrease cholesterol (-31%), increased albumin (+12%) and A/G ratio (+35%), decreased globulin (-15%), increased liver weights and hypertrophy (males)(abs 59%, rel 67%, increased kidney weights (abs 11%, rel 16%) (females: rel 9.5%), no liver necrosis	The observed effects do not indicate a requirement for classification for STOT RE 2.	Exp supporting repeated dose toxicity: oral.002
Oral, 28-day mouse 0.1, 3 and 30 mg/kg bw/day	300 mg/kg bw/day	30 mg/kg bw/day: adverse effects including increased liver weights, hepatocellular hypertrophy, and changes in serum lipids and proteins, increased body weight, decreases in red cell mass (<10%), increased adrenal weight and adrenal cortical hypertrophy, hepatocellular single cell necrosis	Effects which may require classification (almost no information on effect size) as STOT RE including single cell necrosis and changes in serum lipids and proteins were observed at dose levels clearly below the guidance value for STOT RE 2.	Exp supporting repeated dose toxicity: oral.003
Oral, 7-day rat (screening study) 30, 300 and 1000 mg/kg bw/day	1000 mg/kg bw/day	1000 mg/kg bw/day: reduced body weight (males), reduced red cell mass parameters, increase reticulocytes and neutrophils (females), decreases in serum lipids, increased alanine aminotransferase (ALT), aspartate aminotransferase (AST), urea nitrogen (BUN), and Glucose; and decreased sorbitol dehydrogenase (SDH), creatinine, and calcium, increased liver weights, hepatocellular hypertrophy.	As there is almost no information on the effect size, it is difficult to assess the adversity of the observed effects.	Exp supporting repeated dose toxicity: oral.004
Oral, chronic rat Males: 0.1, 1 and 50 mg/kg bw/day Females: 1, 50 and 500 mg/kg bw/day	12.5 mg/kg bw/day	50 mg/kg bw/day: liver: focal cystic degeneration, focal necrosis, centrilobular necrosis, increase liver enzymes, increase in albumin (16%), increase A/G ratio, reduced red cell mass (males) (<10%), reduced red cell mass (females) (<6%), A/G ratio (females) (<6%), 50 mg/kg bw/day: Mild focal necrosis and minimal focal cystic degeneration was also observed in some animals at the one-year interim section (guidance value 25 mg/kg bw/day).	Difficult to assess as the effects at 50 mg/kg bw/day warrant STOT RE classification but the dose is too high whereas at 1 mg/kg bw/day the effects do not warrant classification.	Exp Key repeated dose toxicity: oral.005
Oral, 7-day male mouse	1000 mg/kg	30 mg/kg bw/day: Increased liver and body weight, minimal single	The observed effects do not warrant classification	Exp supporting

Study	STOT RE 2 guidance value	Effects observed (dose in mg/kg bw/day)	RIVM remark	Reference
(screening study) 30 mg/kg bw/day	bw/day	cell necrosis, moderate hypertrophy and increase in mitotic figures	but the tested dose level is clearly below the guidance value for STOT RE 2.	repeated dose toxicity: oral.006
Oral, 90-day mouse 0.1, 0.5 and 5 mg/kg bw/day	100 mg/kg bw/day	5 mg/kg bw/day: liver single cell necrosis (minimal) and other minimal to mild effects	Effects which not require classification as STOT RE were observed at dose levels clearly below the guidance value for STOT RE 2.	Exp supporting repeated dose toxicity: oral.007

Overall, the requirement of STOT RE 2 is difficult to assess because the dose levels tested in mice, with effects that may or may not warrant classification, are clearly below the guidance values and this may be taken as an indication that STOT RE 2 is needed. The effects in the rat are borderline and sometimes difficult to assess due to the large steps in the dose levels.

The registrant does not classify FRD-902 as carcinogenic because the observed increase in liver tumours in females and increases in pancreas and Leydig cell tumours in male rats are not considered relevant to humans. RIVM agrees that there are some species differences with regard to the relevance of these typical tumours for peroxisome proliferators for humans. In line with RAC and IARC, we consider the level of evidence sufficient to show that these tumours are relevant for humans. However, as tumours were only observed in one species, classification as a category 2 carcinogen is justified (suspected human carcinogen).

The available in vitro (OECD TG 471, 476 and 473) and in vivo (OECD TG 474, 475 and 486) genetic toxicity and mutagenicity studies show that FRD-902 is not mutagenic. EFSA (2008) concluded that FRD-902 is non-genotoxic based on the same dataset.

The registrant proposes no classification for reproductive toxicity. In the developmental toxicity study in rats, the only effect on reproduction was early delivery of the offspring at 100 and 1000 mg/kg bw/day. However, the adversity of this effect is uncertain as the offspring was alive and there was no increase in resorptions. In addition, these reproductive effects were observed at dose levels also inducing maternal toxicity. Therefore, classification based on the early delivery is doubtful and in category 2 at most. Other effects include decreased foetal weights at 100 and 1000 mg/kg bw/day and increases in variations at 1000 mg/kg bw/day. These effects in the presence of maternal toxicity do not normally warrant classification.

In the modified one-generation study in mice, postnatal reduced body weight and body weight gain was observed at the highest dose level in the presence of maternal toxicity (liver effects). Secondary delays in development were observed based on time after birth but not based on body weight.

These effects, observed in presence of maternal toxicity, do not normally result in classification.

In Annex I an elaborated overview of the available human health data for FRD-902 is given.

4.2

Conclusion on CMR and STOT RE properties FRD-902

- Carcinogenic: As tumours were only observed in one species, classification as a category 2 carcinogen is justified.
- Mutagenic: The available in vitro and in vivo genetic toxicity and mutagenicity studies show that FRD-902 is not mutagenic.
- Reproductive toxicity: The limited effects observed in presence of maternal toxicity do not normally result in classification.
- STOT RE: The requirement of STOT RE 2 is difficult to assess due to dose levels tested in mice clearly below the guidance values, which may be taken as an Indication that STOT RE 2 is needed. The effects in the rat are borderline and difficult to assess due to the large steps in the dose levels.

4.3

Comparison FRD-902 and APFO

As FRD-902 is used as a replacement of PFOA and its ammonium salt (APFO) for the production of Teflon, a comparison of the toxicological properties of both ammonium salts (FRD-902 and APFO) is considered relevant. An exact comparison is not possible due to differences in applied dose levels. The data in table 5 show that excretion of FRD-902 is much faster in all tested animals compared to APFO. However, comparable PPAR- α effects and tumour types were observed in the available sub-chronic and chronic studies at roughly comparable exposure levels. As comparable effects occurred at comparable external dose levels, but at lower FRD-902 internal concentrations, the interaction of FRD-902 with its toxicological target is probably stronger. Differences are observed in the type of developmental effect between both substances.

Table 5. Comparison of the toxicological properties of FRD-902 and APFO.

		FRD-902	APFO	References
Study type	Parameter	Result	Result	APFO
Kinetics	Half-life mouse	5.2 hours	17-19 days	Lau et al, 2007
	Half-life rat (male)	3.2 hours	4-6 days	Lau et al, 2007
	Half-life monkey (male)	2.3 hours	20.9 days	Butenhof et al, 2004
	Half-life human	unknown	1378 days	Olsen et al, 2007
Acute oral toxicity	LD50 rat	1750 mg/kg bw	250 - 500 mg/kg bw	RAC, 2011
Skin irritation	CLP classification	No classification	Inconclusive	RAC, 2011
Eye irritation	CLP classification	Category 1	Category 1	RAC, 2011

		FRD-902	APFO	References
Study type	Parameter	Result	Result	APFO
90-day study rat	Effects LOAEL	PPAR- α related effects	Liver hypertrophy	Zeilmaker, 2016
	NOAEL/LOAEL	0.1 / 10 mg/kg bw/day	0.06 / 0.64 mg/kg bw/day	Zeilmaker, 2016
Chronic study rat	Effects LOAEL	Increased A/G ratio PPAR- α related effects at higher dose levels	Body weight, liver changes	US-EPA, 2016
	NOAEL/LOAEL	0.1 / 1.0 mg/kg bw/day	1.3 / 14.2 - 16.1 mg/kg bw/day	US-EPA, 2016
Carcinogenicity	Type of tumours	Liver cell adenomas Leydig cell adenomas Pancreas acinar cell tumours	Liver cell adenomas Leydig cell adenomas Pancreas acinar cell adenomas	RAC, 2011
	LOAEL/NOAEL	50 / 1 mg/kg bw/day	15 / 1 mg/kg bw/day	RAC, 2011
Developmental toxicity rat	Type of effects	Early delivery	No developmental effects	RAC, 2011
	LOAEL/NOAEL	100 / 10 mg/kg bw/day	- / 150	RAC, 2011
Generation study mice	Type of effects	No reproductive or developmental effects	Resorptions, stillbirth, postnatal mortality, early preputial separation	RAC, 2011
	LOAEL/NOAEL	- / 5 mg/kg bw/day	1 / - mg/kg bw/day	RAC, 2011

In comparing the toxicity of both substances it is useful to view toxicity as being the result of toxicokinetics and toxicodynamics. As to toxicodynamics, as already stated, the data (in particular the chronic and semichronic studies) indicate that FRD-902 interacts more strongly with its toxicological target than does APFO. As to toxicokinetics, however, the available non-human data for FRD-902 indicate a more favourable profile compared to APFO. As concluded in the present report, human data on the bioaccumulation of FRD-902 are lacking. If human data would confirm that FRD-902 indeed is considerably less bioaccumulative than APFO, overall its long term toxicity for humans can be judged as being lower. It should be noted that for the developmental toxicity endpoint these considerations do not apply. For this endpoint the mouse studies show a clearly lower potency for FRD-902 than for APFO whereas in rats FRD-902 was somewhat more potent (induced early delivery in combination with maternal toxicity at a dose level where APFO induced no effect). Overall with a view to reproductive

toxicity the information on FRD-902 do not normally warrant classification (see sections 4.1 and 4.2), whereas APFO is classified as toxic for the reproduction (category 1B).

4.4 Human health hazards FRD-903

All available toxicological studies were performed with the ammonium salt (FRD-902). Read-across of the toxicological properties of the ammonium salt to the acid is considered justified for systemic effects as after dissolution and dissociation of the acid and the salt the absorption in the intestinal tract and the lungs and distribution over the body of the anion (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate) will be the same. However, local effects to the lung may differ between the two substances as acids normally have a higher irritating effect than neutral salts.

4.5 Human health hazards E1

Only limited toxicological information is available on E1, consisting of a number of study reports provided by Chemours and a summary of the EFSA evaluation of the mutagenicity. Chemours could provide not all studies as some studies contained information on several substances. These are available upon request after redaction to remove all other data. Study summaries of the provided study reports on E1 and further details on the read-across are included in Annex 2.

The available oral kinetic studies indicate low oral absorption of E1. The observed effects after inhalation exposure indicate effects on the central nervous system. This indicates that some absorption can occur via this route. The absence of mortality after high dermal exposure indicates low dermal uptake.

The available acute toxicity studies via the oral (>17000 mg/kg bw), dermal (> 37500 mg/kg bw) and inhalation route (>576000 ppm) show no mortality at high dose levels indicating low overall toxicity and no requirement for classification.

The only repeated dose study is limited to a 10-day inhalation exposure over a period of 12 days and was performed using only male animals. The results show low toxicity limited to CNS depression during exposure. A NOAEC of 25000 ppm was derived.

The available in vitro and in vivo studies show no evidence of a mutagenic potential of E1, as also concluded by EFSA. The Ames test was negative. However, due to the likely evaporation of E1 in the in vitro chromosomal aberration study and the possibly limited amount of E1 in the in vivo inhalation micronucleus test that reached the bone marrow as no change in the PCE/NCE ratio was observed, no conclusion on the mutagenic properties concerning chromosome aberrations can be drawn from these studies.

Read-across

Read-across from FRD-902 to E1 is not justified because of the differences in chemical-physical properties (solid versus liquid with high vapour pressure, acid or salt versus neutral, more lipophilic substance).

In addition, the available toxicological data indicate that E1 is less toxic than FRD-902.

Expert systems including 'Oncologic', 'OECD toolbox' and 'ISS' do not indicate a strong concern for mutagenicity or carcinogenicity.

The two closest analogues identified using the OECD QSAR toolbox, enflurane and isoflurane are used as inhalation anaesthetic used for narcosis at high concentrations and show low toxicity. A range of fluorinated compounds collected from the RepDose database (Frauenhofer) showed limited toxicity with NOECs always above 50 ppm.

Exposure limits

Acceptable Exposure Limit (DuPont): 500 ppm 8 and 12 hour TWA (MSDS, 2007).

4.6

Conclusion on CMR and STOT RE properties E1

Information on the toxicity of E1 is limited but the available information indicates that E1 has a low to very low toxicity. This is supported by the repeated dose toxicity information on some structural analogues.

However, all available studies were performed in male animals and were of limited duration. Overall, the available in vitro and in vivo data on mutagenicity combined with the read-across data show that E1 is unlikely to be mutagenic. In addition, the available data indicate no requirement for classification for acute toxicity and probably STOT RE via inhalation but the requirement for classification for other hazard classes including carcinogenicity, reproductive toxicity and STOT RE via oral exposure is unknown.

4.7

Derivation of a general population exposure limit for FRD-902

4.7.1

Approach

For the derivation of an exposure limit for FRD-902 for the general population the REACH method as described in the "Guidance on information requirements and chemical safety assessment Chapter R.8: Characterisation of dose [concentration]-response for human health" is used (version 2.1 November 2012). Although FRD-902 induces carcinogenicity in experimental animals, the available mutagenicity studies and mechanistic information indicate a non-genotoxic mode of action and therefore a threshold approach can be applied.

The use of an internal dose per ml of serum as dose metric has recently been applied for PFOA by RIVM (Zeilmaker et al, 2016). However, applying this principle to FRD-902 is considered not feasible. The reason for this is that in contrast to the critical studies with PFOA, no information on the serum levels of FRD-902 is available from the critical animal toxicity study. Furthermore, no kinetic model is available for FRD-902 in humans. Moreover, the available data in test animals show quick elimination of FRD-902 (T_{1/2} for elimination from serum in rats 2.8 h in males and 0.2 h in females), which leads to the serum values in the toxicity studies being strongly dependent on the time after the last exposure. Crucially, no information is available regarding the half-life of FRD-902 in humans or regarding serum concentrations in humans. Therefore, the derivation of a limit value on the basis of serum levels as was done for PFOA is unfeasible. Instead, for FRD-902 a method for

deriving a limit value based on the external concentration in air is applied.

Application of the GenX technology leads to emission of FRD-902 via air. As a result, the general population may be exposed to FRD-902 via air, food and/or drinking water. However, no information is currently available regarding levels of FRD-902 in drinking water or food. Therefore, only inhalation exposure is assumed in the present assessment and only a limit value for air is derived. As it cannot be excluded that this exposure will continue for years, a chronic inhalation limit value is determined.

4.7.2 Toxicity studies

The NOAELs derived from the oral repeated dose toxicity studies are summarised in table 6 below.

Table 6. Derived NOAELs for repeated dose toxicity.

Species	Duration	NOAEL mg/kg bw/day	LOAEL mg/kg bw/day	Effects	Reference
Rat	28 days	0.3	30	Reduction in cholesterol	Exp supporting repeated dose toxicity: oral.001
	90 days	0.1	10	A/G ratio increased Reduction in cholesterol Increased liver weight Increased kidney weight	Exp supporting repeated dose toxicity: oral.002
	Chronic	0.1	1	A/G ratio increased	Rae et al, 2015
Mouse	28 days	0.1	3	A/G ratio increased Reduced Hb Liver single cell necrosis	Exp supporting repeated dose toxicity: oral.003
	90 days	0.1	1	Increased liver weight Liver hypertrophy	Exp supporting repeated dose toxicity: oral.007
Rat	Carcinogenicity	1	50	Increase in testis and pancreatic tumours	Rae et al, 2015
	Developmental study	10	100	Early delivery Reduced fetal weights	Developmental toxicity/teratogenicity
Mouse	1-generation study	0.1	0.5	Single cell necrosis in the liver	Exp Supporting Toxicity to reproduction.002

4.7.3 Selection of the most appropriate point of departure

Exposure of the general population due to emissions to ambient air is normally limited to low level of exposures over a long period. The exposure can be intermittent depending on the applied process, release and distribution in the environment. However, based on the available

emission data, only an average concentration per year can be estimated for the general population depending on the distance from the source. Therefore, acute effects after a single high exposure and local effects except local effects on the airways are considered not relevant for the general population in the present case. Accordingly, the assessment is based on effects observed after prolonged low level exposure. For FRD-902 this includes the NOAELs/LOAELs from repeated dose studies, carcinogenicity studies and reproductive toxicity studies.

As no inhalation studies are available with FRD-902 but only oral (gavage) studies, an oral study is used and route-to-route extrapolation is applied for deriving the exposure limit for air. Overall, the NOAEL of 0.1 mg/kg bw/day in the oral chronic study in rats is considered the best available point of departure (POD) for derivation of an exposure limit. This NOAEL is based on an increase in albumin and the albumin/globulin ratio in male rats, an effect that indicates possible immunotoxic effects. This effect was also observed with other PPAR- α inducers and secondary to binding to the PPAR- α receptor (Gervois et al, 2004). As changes in albumin and albumin/globulin ratio also occur in humans after exposure to PPAR- α inducers (Gervois et al, 2004), this effect is considered relevant to humans.

4.7.4 *Inhalation exposure limit*

The NOAEL of 0.1 mg/kg bw/day from the oral (gavage) chronic study is used as POD. Via route-to-route extrapolation the corresponding POD-concentration in air is derived. The chronic study used gavage exposure, meaning that the whole daily dose was applied at once. The possible inhalation of FRD-902 is expected to be evenly distributed over the whole day. Because of the half-life in male rats of only 3 hours, this difference may result in a different internal exposure pattern. The peaks of internal exposure (C_{max}) are expected to be higher under the conditions of the chronic rat study. However, the effect of this difference on the toxicity of FRD-902 in humans is unknown as it is not known whether the peak exposure (C_{max}) or the integrated dose (AUC) determines the critical toxicological effect of FRD-902. No additional safety factor is applied for this difference. In the route-to-route extrapolation, an additional factor for difference in absorption between the oral and the inhalation route is required as the oral absorption has been shown to be 100% but the inhalation absorption is unknown. Available information from comparable substance like PFOA show absorption after inhalation exposure in animals. However, no absorption percentage is provided in the available summaries. Therefore, a default value of 100% is applied in line with the REACH guidance. This is further justified by the absence of metabolism showing that first pass effects are not relevant. Route-to-route extrapolation was performed by dividing the point of departure of 0.1 mg/kg bw/day by 1.15 m³/kg bw/day¹⁸ resulting in a POD for the air concentration of 0.087 mg/m³.

Besides this allometric scaling factor of 4, normally an interspecies factor of 2.5 for remaining toxicokinetic and toxicodynamic differences

¹⁸ Inhalation volume per kg bw per day in rats which is compatible with a factor 0.25 for allometric scaling from rats to humans, 70 kg bw and 20 m³/day as the daily ventilation volume for humans: (20 m³/day * 4) / 70 kg bw = 1.15 m³/kg bw/day

and an intraspecies factor of 10 are used in agreement with the REACH guidance.

Additional factor for potential kinetic difference

However, there is concern regarding the potential difference in half-lives between the tested animal species and humans. FRD-902 is used as a replacement of PFOA and is also a fully fluorinated carboxylic acid. The half-life of PFOA in humans is much longer than those in all tested animal species (mouse, rat, monkey) (Zeilmaker et al, 2016) probably due to stronger reabsorption from the lumen of the kidney back into the blood by organic anion transporters (OATs) (Yang et al, 2010). There are genetic differences in OATs between humans and the tested animal species (Yang et al, 2010). As FRD-902 is also an anion, this mechanism cannot be excluded. The elimination of FRD-902 was tested in three animal species (Gannon et al, 2016) and the results show that in these species the half-life of FRD-902 was clearly shorter than those of PFOA, suggesting that for FRD-902 reabsorption by OATs is lower or absent entirely, at least in these species. However, because of the genetic differences of the OATs between the tested animal species and humans (Yang et al, 2010) this cannot be directly extrapolated to humans. Thus, for humans the involvement of OATs in the elimination of FRD-902 in cannot be excluded. Moreover, contrary to other perfluorinated compounds, no data are available for FRD-902 to confirm whether the fast elimination and absence of accumulation as seen in several animal species also applies to humans.

In view of the above, an additional toxicokinetic assessment factor is applied to take into account the uncertainty in the human elimination rate of FRD-902. This additional toxicokinetic factor is based on the difference in half-lives between cynomolgus monkeys and humans as determined for PFOA. Using a half-life of 1378 days in humans (mainly males)(Olsen et al, 2007) and of 20.9 days in male cynomolgus monkeys (Butenhoff et al, 2004), leads to an additional toxicokinetic factor of 66 (1378 / 20.9).

The PFOA half-life in male cynomolgus monkey is used in deriving this additional factor instead of the half-life for PFOA in male rats (the species used in the pivotal chronic study) because for FRD-902 the half-lives in male rats and cynomolgus monkeys were similar in size whereas for PFOA the half-life in cynomolgus monkeys is much longer than that in male rats (20.9 days in male cynomolgus monkeys versus 6-7 days in male rats). This indicates that for FRD-902 the use of the factor between male rats and humans for PFOA is not appropriate.

Interspecies remaining difference

Interspecies extrapolation corrects for the differences in the sensitivity between experimental animals and humans. This covers differences in toxicodynamics and toxicokinetics. Some of the toxicokinetic differences can be explained by body size in relation to the basal metabolic rate. The latter is linked to the inhalation volume per kg bw. By default, in the extrapolation from animals to humans an interspecies correction for metabolic rate is applied (a factor of 4 in case of rats), as described above. An additional factor of 2.5 for remaining differences, i.e. toxicokinetic differences not related to metabolic rate (small part) and

toxicodynamic differences (larger part). As the REACH guidance points out, in case substance-specific information shows specific susceptibility differences between species, which are not related to differences in basal metabolic rate (not covered by allometric scaling), the additional factor of 2.5 for 'remaining differences' should be modified accordingly. The potential difference in half-life of FRD-902 between the tested animal species and humans is a potential difference in toxicokinetics which is probably not related to the metabolic rate.

Therefore, the calculated potential difference in half-life is used to replace the toxicokinetic part of the additional factor of 2.5. As the toxicodynamic part is the larger part of the remaining difference, a factor of 1.8 is applied as the remaining factor for toxicodynamic interspecies extrapolation. The factor of 1.8 was selected as being the larger part of the 2.5 factor which is not quantified in the ECHA guidance R.8.

No assessment factor for duration of exposure is applied as the point of departure is a chronic study. In addition, no factor is applied for the dose-response relationship as the point of departure is a NOAEL. Also, no factor is applied for quality of the database as repeated dose toxicity studies in two species, a carcinogenicity study and reproductive toxicity studies are available.

Overall, the following assessment factors are applied:

• Additional factor for potential kinetic difference	66
• Interspecies remaining toxicodynamic difference	1.8
• Intraspecies	10

Therefore, the overall assessment factor is 1188. Combining this assessment factor with the point of departure of 0.087 mg/m^3 , results in an chronic inhalation exposure limit of 73 ng/m^3 .

Although local effects on the lung due to the irritating properties of FRD-902 at the inhalation point of departure of 0.087 mg/m^3 cannot be excluded, it is considered unlikely that such effects could be critical for the limit value as the derivation of limit values based on local irritating effects does not require additional assessment factors for possible differences in accumulation. Therefore, the limit value of 73 ng/m^3 is considered to be also protective for local irritating effects.

Using the additional toxicokinetic factor as above represents a pragmatic worst-case approach based on the data as currently available. Additional information on the bioaccumulation of FRD-902 in humans and on the inhalatory absorption rate would allow derivation of an improved exposure limit.

4.8

Derivation of a general population exposure limit for FRD-903

All available toxicological studies were performed with the ammonium salt (FRD-902). Read-across of the toxicological properties of the ammonium salt to the acid is considered justified for systemic effects as after dissolution and dissociation of the acid and the salt the absorption in the intestinal tract and the lungs and distribution over the body of the

anion (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate) will be the same.

Local effects to the upper airways and lungs may differ between FRD-902 and FRD-903 as acids normally have a higher irritating effect than neutral salts. Thus the derived limit value in air for FRD-902 might underestimate the local toxicity of FRD-903. However, it is considered unlikely that such effects are determinative for the limit value as the derivation of limit values based on local irritating effects does not require additional assessment factors for possible differences in accumulation. Therefore, the limit value of 73 ng/m³ is considered to adequately cover the local irritating effects of FRD-903 and FRD-902.

4.9 Derivation of a general population exposure limit for E1

As indicated before, the information on the toxicity of E1 is limited and no studies were performed using female animals. However, the available information indicates that E1 has a low to very low toxicity. This is supported by the repeated dose toxicity information on some structural analogues. However, the data are insufficient for deriving an inhalation exposure limit.

5 Indicative concentrations around the Chemours plant due to FRD-903 and E1 emission

As indicated in section 2.2, FRD-903 and E1 are emitted to air from the Teflon PTFE and from the Teflon FEP plants (see tables 7 to 10). The presented data are based on the maximum emission indicated in the permits, the emission recorded in the Electronic Environmental Year report of Chemours and additional data provided by Chemours.

Table 7. Emissions to air of FRD-903 for both plants in kg/year.

Year	Permitted PTFE	Recorded PTFE	Permitted FEP	Recorded FEP
2012	600	197	40	10
2013	600	292	40	27
2014	600	386	40	31
2015	600	288	40	27

Table 8. Emissions to air of FRD-903 per stack for both plants in kg/year.

		Emissions to air FRD-903		
		2013	2014	2015
FEP	TL20 scrubber	5	6	6
	TL33 membrane unit	12	14	12
	TL34 vacuum filter 1	1	2	1
	TL35 vacuum filter 2 and 3	8	9	8
	Total FEP	27	31	27
PTFE	TL05 dryer granular	24	19	20
	TL10a waxtrap	13	16	12
	TL10b wash separators	13	17	13
	TL12 scrubber	242	334	243
	Total PTFE	292	386	288

Table 9. Emissions to air of E1 for both plants in kg/year.

Year	Permitted PTFE	Recorded PTFE	Permitted FEP	Recorded FEP
2012	750	205	450	11
2013	750	293	450	42
2014	750	390	450	48
2015	750	288	450	46

Table 10. Emissions to air of E1 per stack for both plants in kg/year.

		Emissions to air E1		
		2013	2014	2015
FEP	TL20 scrubber	7	8	7
	TL31 flotation tanks	25	29	29
	TL36 vacuum system	10	11	11
	Total FEP	42	48	46
PTFE	TL01 vacuum granular claaif	11	9	9

		Emissions to air E1		
		2013	2014	2015
	TL05 dryer granular	1	1	1
	TL10a waxtrap	17	22	17
	TL10b wash separators	18	23	17
	TL12 scrubber	227	313	228
	TL13a dryer east	10	12	9
	TL13b dryer west	9	10	8
	Total PTFE	293	390	288

The characteristics of the stacks are copied from the request for revision of the permit of 2013. These characteristics are presented in table 11. At the moment the calculations were carried out no information about the exact locations of all stacks was available. It was assumed all stacks in the FEP-plant have the same location as TL20 and all stacks in the FTPE plant as TL12. For FEP TL36 characteristics were invalid, instead TL20 characteristics were used. Same for FTPE TL01, here TL12 characteristics were used. Since not all information was available these calculations should be considered as indicative.

Table 11. Reported emission characteristics of the stacks (request for revision of the permit of 2013).

Plant	FEP						
Stackname	TL20	TL31	TL33	TL34	TL35	TL36	TL37
x-coordinate RDM (m)	109817						
y-coordinate RDM (m)	425858						
Stack height (m)	28	19	11.7	0	0	40	5.9
diameter (m)	0.4	0.08	0.434	0.08	0.21	0.08	0.125
temperature (K)	353	323	293	293	293	373	293
flow rate (Nm ³ /u)	700	200	250	150	850		50
heat content (Mw)	0.016	0.003	0.000	0.000	0.002		0.000
Plant	PTFE						
Stackname	TL01	TL5	TL10a	TL10b	TL12	TL13a	TL13b
x-coordinate RDM (m)					109726		
y-coordinate RDM (m)					425865		
Stack height (m)		12	12	12	20	14.7	5.6
diameter (m)		0.36	0.25	0.5	0.8	0.68	0.4
temperature (K)		333	293	293	323	318	333
flow rate (Nm ³ /u)		6500	2000	2500	20000	1900	1750
heat content (Mw)		0.106	0.004	0.005	0.253	0.021	0.028

Based on the permitted and recorded (2014) emissions to air the air concentrations around the Chemours plant are calculated using the RIVM model OPS-PRO version 4.5.0¹⁹. As no information on particle-size,

¹⁹ <http://www.rivm.nl/media/ops/v4.5.0/OPS-model-v4.5.0.pdf>

coagulation or deposition is available, in the calculations it is assumed all substance maintains in the air without any (wet or dry) deposition. This can be seen as a worst case. The distribution is calculated in a 50 x 50 km grid. Within this grid, the concentration is calculated in cells of 100 x 100 m. The calculated result does not give the exact concentration at a certain point, but is the average concentration of the cell.

The calculated air concentrations in the nearest populated areas (along the dike at the other side of the river) are around 20 ng/m³ (permitted emissions) versus 15 ng/m³ (recorded emissions) for FRD-903 and around 40 ng/m³ (permitted emissions) versus 20 ng/m³ (recorded emissions) for E1.

6 Possible health effects in residents in the vicinity of the Chemours plant

In chapter 4, the available human health effects information on FRD-902/903 is evaluated, based on which a chronic inhalation exposure limit of 73 ng/m³ is derived (paragraph 4.6.4). In chapter 5, the year-average air concentrations were calculated, in first instance based on the permitted emissions and, secondly also for the recorded emission for 2014. This led to estimated concentrations in air of about 20 ng/m³ for the nearest populated areas (along the dike at the opposite side of the river) and lower concentrations at greater distances from the plant based on the permitted concentrations. Based on the recorded emissions for 2014 the estimated concentrations for the nearest populated areas are about 15 ng/m³.

Comparing these concentrations with the limit value of 73 ng/m³ leads to the conclusion that based on the available data, no health risk is expected for people living in the vicinity of the Chemours Dordrecht plant due to exposure to FRD-903.

To illustrate the results, figure 1 shows the calculated concentration FRD-903 in air based on the recorded emission in 2014 compared to the exposure limit derived in this report. The data from 2014 have been used, because in this year the highest emission was recorded. The figure shows that only directly next to the stack, air concentrations above 73 ng/m³ are calculated. Annex 3 presents the calculated concentration FRD-903 in air based on the permitted emissions.

In chapter 4 also the available human health effects information on E1 is evaluated. The conclusion was that limited toxicological information and structure-activity relations indicate that this chemical has low toxic potential only. However, the data are insufficient for deriving an inhalation exposure limit. In chapter 5, the year-average air concentrations for E1 were calculated based on the permitted emissions. This led to estimated concentrations in air of about 40 ng/m³ for the nearest populated areas (along the dike at the opposite side of the river) and lower concentrations at greater distances from the plant. Based on recorded emissions for 2014 the estimated concentrations for the nearest populated areas are about 20 ng/m³.

Due to the insufficient health effects information available for E1, these concentrations cannot be evaluated as to the possible health risk they might pose for people living in the vicinity of the Chemours plant in Dordrecht.



Figure 1. Calculated air concentrations FRD-903 based on the recorded emissions (in ng/m³).

7 Conclusions

In chapter 3 of this report, on PBT-properties, the conclusion is that it cannot be excluded that the GenX related substances meet the PBT/vPvB criteria. All evaluated substances (FRD-903, FRD-902 and E1) are perfluorinated compounds and should therefore be regarded as certainly P/vP. Since FRD-903 and FRD-902 in animals are more rapidly eliminated than PFOA, it is expected that both substances bioaccumulate less than PFOA. However, it is not possible to reach a conclusion on the human bioaccumulation potential in absence of data on the human clearance time. For the substance E1, insufficient information is available to draw a conclusion about the bioaccumulation potential for FRD-902 and FRD-903. Since E1 contains no hydrophilic group, the human clearance time of the substance and the bioaccumulation potential are expected to be higher than for PFOA, although E1 has the potential to be excreted via exhalation. Finally, FRD-903 and FRD-902 are considered less toxic compared to PFOA. However, no definitive conclusion on the T criteria can be reached. E1 will most likely not meet the T criteria.

Chapter 4 evaluates the CMR and STOT RE properties of the three substances. It is concluded that classification as carcinogenic category 2 (suspected human carcinogen) is justified for FRD-902. The available studies show that both substances are not mutagenic. On reproductive toxicity the limited effects observed in presence of maternal toxicity do not normally result in classification, whereas PFOA is classified as toxic for the reproduction (category 1B). The requirement of STOT RE 2 (like liver and kidney) is difficult to assess due to dose levels tested in mice clearly below the guidance values, which may be taken as an indication that STOT RE 2 is needed. The effects in the rat are borderline and difficult to assess due to the large steps in the dose levels. Effects on the liver are observed at the similar dose levels for FRD-902 and PFOA.

All available toxicological studies were performed with the ammonium salt (FRD-902). Read-across of the toxicological properties of the ammonium salt to the acid is considered justified for systemic effects as after dissolution and dissociation of the acid and the salt the absorption in the intestinal tract and the lungs and distribution over the body of the anion (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate) will be the same. However, local effects to the lung may differ between the two substances as acids normally have a higher irritating effect than neutral salts.

Information on the toxicity of E1 is limited but the available information indicates that E1 has a low to very low toxicity. This is supported by the repeated dose toxicity information on some structural analogues. Contrary to what is usual in toxicology, all available studies with E1 were performed in male animals only. In addition only studies of limited duration are available. Overall, the available in vitro and in vivo data on mutagenicity combined with the read-across data show that E1 is unlikely to be mutagenic. In addition, the available data indicate no requirement for classification for acute toxicity and probably STOT RE

via inhalation but the requirement for classification for other hazard classes including carcinogenicity, reproductive toxicity and STOT RE via oral exposure is unknown.

Chapter 4 completes with the derivation of an chronic inhalation exposure limit of 73 ng/m^3 for FRD-903 and FRD-902 which includes an additional toxicokinetic factor in a pragmatic worst-case approach. The available information on the toxicity of E1 is limited. The data are insufficient for deriving an inhalation exposure limit.

Based on the permitted and recorded emission to air, the air concentrations around the Chemours plant are calculated in chapter 5. Comparing the calculated concentrations in air with the limit value of 73 ng/m^3 in chapter 6 leads to the conclusion that based on the available data, no health risks are expected for people living in the vicinity of the Chemours Dordrecht plant due to exposure to FRD-903. Due to the insufficient health effects information available for E1, these concentrations cannot be evaluated as to the possible health risk they might pose for people living in the vicinity of the Chemours plant in Dordrecht.

8 Acknowledgements

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Annex 1. Human health toxicity FRD-902

Introduction

Most study summaries were copied from the robust study summaries in the registration dossier. The summaries were checked and conclusions by the registrant to which RIVM did not agree or were questioned were removed or it was added that this was a conclusion of the registrant. No attempt was made to have an RIVM conclusion on a parameter if the parameter was not determinative for the derivation of the NOAEL. The RIVM conclusion on the NOAEL is included at the end of each study summary. In addition, the study reports of the key studies (90-day mouse, 90-day rat and chronic rat) were provided by Chemours. A comparison of the summaries in the registration dossier with the study report showed that the summaries were copied from the study report. In addition, the results were compared with the detailed study results and additional details were added where necessary.

A1.1 Kinetics FRD-902

Gannon et al. (2016) tested the absorption, distribution, metabolism and excretion (ADME) and kinetics of FRD-902 (the ammonium salt) in rats, mice and cynomolgus monkeys. Pharmacokinetics was determined by measuring in blood samples from rats and mice at multiple time points after a single oral dosing at 10 or 30 mg/kg. In addition, pharmacokinetics after single intravenous exposure (10 mg/kg) were measured at multiple time points up to 7 days in rats and up to 21 days in cynomolgus monkeys. ADME parameters were measured in tissue and excreta up to 168 hours after oral dosing in mice (dose: 3 mg/kg) and in rats (dose: 30 mg/kg). A hepatocyte metabolism test indicated that FRD-902 is not metabolized by rat hepatocytes, which was supported by the absence of metabolites and the complete recovery of the dosed FRD-902 in rat and mouse urine. As shown in table A1, FRD-902 is rapidly absorbed after oral exposure and shows biphasic elimination with a very rapid alpha-phase and a slower beta-phase elimination. The alpha-phase elimination half-life was faster in female rats compared to male rats. Furthermore, it is mentioned in the publication that because the urinary elimination rate is very rapid (nearly the entire dose was eliminated within 12-24 hours), the sex difference observed in the plasma kinetics was not readily apparent in the urine kinetics. No test substance was detected in the blood of monkeys 16 days after dosing probably due to the much slower elimination in the beta-phase. For both rats and monkeys the alpha phase was very rapid and the contribution of the beta-phase was considered negligible. Therefore, the authors concluded that the beta phase elimination did not contribute to potential accumulation after multiple dosing in rats or monkeys. Nearly the whole administered dose was eliminated in the urine (table A2) in rats and mice. A small amount of the test substance was recovered in the faeces, but this was likely due to contamination of the faeces with urine. Tissues were not analyzed, because at the conclusion of the study (at 168 h) the entire dose was recovered in the urine, faeces, and cage wash. No metabolites were found.

Pharmacokinetics differed between rats and mice, with a slower elimination rate in mice compared to rats. The elimination rate in monkeys was more similar to male rats.

Table A1. Pharmacokinetic parameters of ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (FRD-902) as presented in Gannon et al 2016.

heptanfluoropropoxy)-propanoate (FRD-902) as presented in Gannon et al 2016.

Constant	Units	Rat, intravenous		Rat, oral		Mouse, oral		Cynomolgus monkey, intravenous	
		Male	Female	Male	Female	Male	Female	Male	Female
Absorption									
Rate constant (k_a)	1/h	NA	NA	3.30	1.52	3.83	3.11	NA	NA
Time	h	NA	NA	0.21	0.46	0.18	0.22	NA	NA
Alpha phase									
Elimination rate constant	1/h	0.20	1.72	0.25	2.78	0.12	0.15	0.30	0.37
Half-life	h	3.6	0.4	2.8	0.2	5.8	4.6	2.3	1.9
Beta phase									
Rate	1/h	7.8E-03	3.1E-02	9.6E-03	1.0E-02	1.9E-02	2.9E-02	1.1E-02	8.7E-03
Half-life	h	89.1	22.6	72.2	67.4	36.9	24.2	64.1	79.6
Volume of distribution									
Central	L/kg	0.168	0.178	0.142	0.057	0.117	0.148	0.068	0.056
Peripheral	L/kg	0.155	1.508	0.161	2.462	0.130	0.078	0.029	0.021

Table A2. Material balance of ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (FRD-902) dosing in rats and mice, as presented in Gannon et al 2016.

	Rat (30 mg/kg)				Mouse (3 mg/kg)			
	Male		Female		Male		Female	
	Mean (%)	SD (%)	Mean (%)	SD (%)	Mean (%)	SD (%)	Mean (%)	SD (%)
Urine	103	2.7	100	6.4	90	6.9	92	6.0
Feces	1	1.0	1	0.6	2	1.0	2	0.6
Cage wash	1	0.5	5	5.1	10	4.0	6	3.2
Total	105	2.2	106	1.4	101	3.2	99	3.2

In the REACH registration dossier, 10 studies in experimental animals and two *in vitro* studies were available for basic toxicokinetics. The *in vitro* studies were carried out with rat hepatocytes (Exp Supporting Basic Toxicokinetics.012) and trout hepatocytes (Exp Supporting Basic Toxicokinetics.011) and showed no indication of metabolism. Several

studies included in the registration were published by Gannon et al (2016) and are described above. Other studies in orally exposed rats (doses ranging from 10 – 30 mg/kg) showed that the test compound was almost completely eliminated in urine and reported half-lives of between 13.2 and 18.8 hours, clearance times (98.4%) at doses of 10 and 30 mg/kg of 12 h and 22 h for male rats, and of 4 h and 8 h for female rats, respectively. No test compound was recovered in the fat of male and female rats and no test compound was recovered in the liver of female rats. In male rats, the tissue:plasma ratio in the liver was 2.2 at a dose of 10 mg/kg, and 0.8 at a dose of 30 mg/kg, respectively (Exp Supporting Basic Toxicokinetics.008).

In another study (Exp Supporting Basic Toxicokinetics.007), rats were exposed by intravenous injection with 10 or 50 mg/kg. Reported clearance times were 22 h and 3 h for male and female rats, respectively, at a dose of 10 mg/kg. At a dose of 50 mg/kg, reported clearance times were 17 hours and 4 hours for male and female rats, respectively.

One additional study in mice was available (Exp Supporting Basic Toxicokinetics.010), in which mice were given a single oral dose of 10 or 30 mg/kg. At 10 mg/kg, the plasma clearance time was 143 h and 57 h for male and female mice, respectively. At 30 mg/kg, the plasma clearance time was 139 h and 62 h for male and female mice, respectively. The tissue:plasma ratio for fat was >0.1 in male rats exposed to 30 mg/kg. In male rats in the 10 mg/kg dose group, no test substance was detected in fat. The tissue:plasma ratio for the liver was 0.5 for male rats in both the 10 mg/kg and 30 mg/kg dose groups. In female rats, no test substance was detected in fat or liver.

One study in cynomolgus monkeys is reported in the registration dossier (Exp Supporting Basic Toxicokinetics.003). From the results presented it could not be determined whether these data also refer to the Gannon et al (2016) study. Therefore, the study report in cynomolgus monkeys is presented here as well. Monkeys were exposed to 10 mg/kg by a single intravenous injection. Blood was collected at multiple time points (approximately 0.083 (5 min), 0.167 (10 min), 0.25 (15 min), 0.5 (30 min), 1, 2, 4, 8, 12, and 24 hours post dose). Additional blood samples were collected once daily on day 3 – 21. Half-lives at a time interval of 0-12 h were 1.8 h and 1.6 h for male and female monkeys, respectively (Table 5). Clearance times were reported to be 11 hours for males and 10 hours for females.

Table A3. Half-life in cynomolgus monkeys as reported in the REACH registration dossier for ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate; study report Exp. Supporting Basic toxicokinetics.003.

Half-life of Test Substance in primate plasma over the time interval corresponding to clearance time			
	Time Interval (hr)	Lambda (1/hr)	Half-life (hr)
Male	0-12	0.3845	1.8
	4-12	0.2666	2.6
Female	0-12	0.4288	1.6
	4-12	0.3047	2.3

One study on toxicokinetic data in rats after prenatal exposure was available in the registration dossier (Exp Supporting Basic Toxicokinetics.006). Pregnant rats were exposed to a daily dose of 5, 10, 100 or 1000 mg/kg/day by oral gavage during gestational days (GD) 6 – 20. Plasma concentrations were measured in the fetuses on GD20, in dams on GD20, and additionally on GD6 in dams in the highest exposure group (1000 mg/kg/day). A linear dose-plasma concentration relation was observed between 5 and 100 mg/kg/day, levelling off at 1000 mg/kg/day. The mean plasma concentration on GD20 was less than that on GD6, indicating that a steady state was achieved by GD6 and no accumulation occurred in the dams between GD6 and GD20. The plasma concentration in fetuses (pooled concentration) was approximately one-third of the plasma concentration in the dam at GD20.

One report on dermal absorption of FRD-902 (purity 86%) was available in the registration dossier performed according to OECD TG 428 in 2008. Dermal absorption was studied in a static diffusion cell setup with rat and human skin at a concentration of 124 mg/ml. In rat skin, a lag time of 0.82 ± 0.77 hours was observed and in human skin the observed lag time was 1.73 ± 1.01 hours. Steady state penetration was 70 ± 5.3 ug/cm²/h and Kp was $5.7E-4 \pm 4.3E-5$ cm/h in rat skin. In human skin, steady state penetration was 6.2 ± 5.3 ug/cm²/h and Kp was $5.0E-5 \pm 4.3E-5$ cm/h.

Conclusions on ADME.

The available data indicate that FRD-902 is quickly absorbed after oral and absorbed after dermal exposure, not metabolized, and eliminated almost completely within approximately 24 hours via urine in rats, mice and monkeys. The substance distributes into the fetus. The elimination was significantly higher in female rats compared to male rats but no such difference was observed in mice and cynomolgus monkeys.

A1.2 Acute toxicity

Oral

Two studies in rats and one study in mice were available from the registration dossier on acute toxicity by the oral exposure route. The studies were performed according to OECD Guideline 425 and EPA OPPTS 870.1100. Test substance (86% purity) was applied by oral

gavage at doses of 175, 550, 1750, and 5000 mg/kg for rats and 175, 550 and 1750 mg/kg for mice. Animals were observed during 14 days and then necropsied.

All female rats in the highest dose group (5000 mg/kg) died; one at the day of dosing, one the following day, and one 2 days after dosing. In these rats, lung discoloration, discoloration of the mandibular lymph nodes, and liver were found. Hair loss, high posture, stained fur/skin, wet fur, lethargy, clear ocular discharge, prostrate posture, partially closed eyes, and/or salivation were observed in all female rats. However, with the exception of hair loss, these clinical symptoms had reversed after day 2. No body weight loss was observed. The oral LD50 for female rats was 3129 mg/kg (Exp Support Acute Tox: oral.001).

All male rats in the highest dose group (5000 mg/kg) and one male rat in the 1750 mg/kg dose group died. These rats showed lethargy, skin stain, expanded lungs, eye discoloration and stomach discoloration. One rat in the 175 mg/kg dose group also showed lethargy. Other clinical findings in the 550 and 1750 mg/kg dose groups were wet fur and stained fur or skin, which reversed after 2 days post-dosing. No body weight loss was observed. The oral LD50 for male rats was 1750 mg/kg, with 95% profile likelihood confidence interval 1239 – 4450 mg/kg. This study was selected by the registrant as the key study for acute toxicity after oral exposure (Exp Key Acute Tox: oral.003).

In mice, all mice in the highest dose group (1750 mg/kg) died. These mice exhibited lethargy and low posture. One mouse in the 550 mg/kg dose group exhibited wet fur. No effects on body weight were observed. A number of gross lesions was observed, including discoloration of the lungs, cyst in ovaries of one mouse, and skin stain in two mice, but these lesions were considered nonspecific by the registrant. The oral LD50 for mice was 1030 mg/kg (Exp Support Acute Tox: oral.002).

Three additional studies in male rats were available in the registration dossier, but have been marked as 'not reliable' by the registrant because the test substance composition was insufficiently defined.

Based on the key study in male rats with an LD50 of 1750 mg/kg bw, classification as Acute Tox 4; H302 is warranted.

Inhalation

One study on acute inhalation toxicity was available in the registration dossier (Acute Toxicity: inhalation). The study was performed according to OECD Guideline 403. Rats were nose-only exposed to aerosol concentrations of 13, 100, and 5200 mg/m³ for 4 hours. Animals were observed for 2 – 14 days after exposure and necropsy and microscopic evaluation of the respiratory tract tissues were performed, except in the highest dose group. No mortality was observed. Rats in the highest dose group (5200 mg/m³) showed red discharge around the eyes, nose and mouth, and red stained faces that lasted for 2 days. Rats in the 100 mg/m³ dose group also showed red nasal discharge immediately after exposure. No mortality, other clinical signs of toxicity or substance-related microscopic findings were observed in any dose group in this study (however, microscopic analysis was not performed in the 5200

mg/m³ dose group). Body weight loss between 2.5% - 6.8% as compared to controls was observed in rats in the highest dose group. Rats in the other dose groups also showed minor decreases in body weight, however, a similar minor decrease in body weight was also observed in the control group. The LC50 for acute inhalation toxicity in male rats was reported as > 5200 mg/m³. Based on this study classification is not warranted.

Dermal

Two acute toxicity studies for the dermal exposure route were available in the registration dossier; one in rabbits and one in rats.

Rabbits were exposed by occlusive patch for 24 hours to a dose of 5000 mg/kg. No mortality was observed (2 rabbits were used in the study). There was no mortality. Moderate to mild erythema was observed that lasted for 10 days after exposure and then decreased. Epidermal scaling and sloughing was observed in both rabbits from 6 to 13 days after application and one rabbit showed a small area of necrosis outside the test area (attributed to test substance running out of the test site) between 2 - 6 days after exposure. An ALD of > 5000 mg/kg was reported (Exp Supporting Acute Toxicity: dermal.002).

The study in rats was performed according to international guidelines (OECD Guideline 402 / EPA OPPTS 870.1200 / EEC, Method B.3 Directive 92/69/EEC) and included semi-occlusive application for 24 hours, followed by wash-off, post-exposure observation for 14 days and necropsy. The applied dose was 5000 mg/kg (Exp Key Acute Toxicity: dermal.001). No mortality was observed. Reversible local effects were observed on the treated skin.

Based on these studies classification is not warranted.

A1.3 Irritation and corrosion

The available skin irritation study according to OECD TG 404 (Skin irritation/corrosion) showed limited and reversible erythema (score 1 or 2) at 1 hour after removal of FRD-902 (86% purity). Based on this study classification for skin irritation is not warranted.

The available eye irritation study according to OECD TG 405 (Eye irritation) showed irreversible effects in the tested rabbit including cornea opacity, iritis and conjunctival chemosis and discharge. The rabbit was euthanized the day after treatment for humane reasons. Based on this study classification as Eye Damage 1; H318 is warranted.

A1.4 Sensitisation

In a LLNA test according to OECD TG 429 (Exp Key Skin sensitisation.002), FRD-902 dissolved in dimethylformamide at 0, 5, 25, 50 and 100% induced no increase in the stimulation index above 3. Therefore, this test was considered negative and does not warrant classification as skin sensitiser.

A second LLNA test was available in the registration dossier in which a crude and undefined mixture was tested and positive with an EC3 of 37%. However, the relation of the tested substance with the marketed

substance was questioned. Therefore, based on the first test the marketed substance need not to be classified for skin sensitisation.

A1.5 Mutagenicity

In an Ames test according to OECD TG 471 (Exp Key genetic toxicity in vitro.001) up to 5000 ug/plate using plate incorporation, FRD-902 was negative with and without metabolic activation. A comparable study (Exp supporting in genetic toxicity in vitro.003) with a test substance which was not sufficiently characterised according to the registrant, was also negative. In a mammalian cell gene mutation assay according to OECD TG 476 (Exp Key genetic toxicity in vitro.002) in which the pH was adjusted to neutral, FRD-902 was negative with and without metabolic activation. In an in vitro mammalian chromosome aberration test according to OECD TG 473 (Exp Key genetic toxicity in vitro.005), FRD-902 was negative after 4 and 20 hour exposure without metabolic activation but positive after 4 hour exposure with metabolic activation at the highest exposure level of 3471 ug/ml. In the first test, there was no statistically significant increase at this concentration but the control value for numerical aberrations was outside the historical control range. In a confirmatory trial, the structural and numerical aberrations were increased compared to the concurrent control at the highest dose level. A comparable study (Exp supporting in genetic toxicity in vitro.004) with a test substance which was not sufficiently characterised according to the registrant, was negative.

In a mouse micronucleus test according to OECD TG 474 (Exp Key genetic toxicity in vivo.001) at dose levels up to 1300 mg FRD-902/kg bw by gavage, a reduction in PCE/EC was observed in the bone marrow, showing that the substance reaches the bone marrow, but no increase in micronucleated PCE. Some mortality was observed at the highest dose. In a mouse chromosome aberration test according to OECD TG 475 (Exp Key genetic toxicity in vivo.003) at dose levels up to 1300 mg FRD-902/kg bw by gavage, a decrease in the mitotic index of bone marrow cells was observed but no increase in structural or numerical chromosome aberrations. Some mortality was observed at the highest dose. In a rat unscheduled DNA synthesis test according to OECD TG 486 at dose levels up to 2000 mg FRD-902/kg bw by gavage, no increase in net grains per nucleus was observed.

The available in vitro and in vivo genetic toxicity and mutagenicity studies show that FRD-902 is not mutagenic. EFSA (2009) concluded that FRD-902 is non-genotoxic based on the same dataset.

A1.6 Carcinogenicity

In a combined chronic and carcinogenicity study performed according to OECD Guideline 453, 80 rats per dose and sex were exposed to FRD-902 (purity 84%) by gavage (water). The dose levels were males: 0.1, 1, 50 mg/kg bw/day and females: 1, 50, 500 mg/kg bw/day. Interim necropsy was performed on 10 animals after 12 months. The remaining animals were necropsied after 101 weeks (females) or 104 weeks (males)(Rae et al, 2015).

In high dose females, a significant increased incidence of hepatocellular adenoma and hepatocellular carcinoma was observed. In high dose males, a statistically significant increase was observed in the incidence of pancreatic acinar cell adenoma/carcinoma combined, but not adenoma or carcinoma alone. The incidence of interstitial cell adenoma of the testes was increased in males at 50 mg/kg/day, and one interstitial cell adenoma was also present in one male in the 50 mg/kg/day group at the interim necropsy. Also the incidence of interstitial cell hyperplasia was increased in this group and outside the historical control range. These findings were not statistically significant, amongst others due to a relatively high incidence of these lesions in the controls. The increase in uterus stromal polyps was within the range of the historical controls. Therefore, it is uncertain whether this statistical significant increase in polyps is substance related.

Table A4. Tumor incidences and related histological changes in the OECD 453 study in rats.

Tumor type	Sex	Hist control	Control	Low	Mid	High
Hepatocellular adenoma (%)	Females	0-5%	0	0	0	11 (15.71%)*
	Males		1	2	1	1
Hepatocellular carcinoma	Females	0-1.7%	0	0	0	4 (5.71%)*
	Males		1	0	0	2
Pancreatic acinar cell adenoma	Males	0-5%	0	1	0	3 (4.29%)
Pancreatic acinar cell carcinoma	Males	0-1.7%	0	0	0	2 (2.86%)
Combined acinar cell tumors	Males		0	1	0	5*
Interstitial cell adenoma testes	Males	0-8.3%	4	4	1	8 (11.43%)
Interstitial cell hyperplasia	Males	0-8.3%	7	7	3	15 (21.4%)
Uterine stromal polyps	Females	0-13.8%	1	2	1	7 (10%)*

* Statistically significant in at least 2/3 statistical tests

It was suggested by the study authors that the observed increase in tumors was induced by non-genotoxic peroxisome proliferation, which is specific for rodents. We agree that the available data do indicate a non-genotoxic mechanism. However, we do not currently agree, as further substantiated in the chapter on the mode of action, that it is sufficiently shown that these types of tumours via this mechanism are not relevant for humans. The NOAEL for carcinogenicity is 1 mg/kg bw/day in males based on an increase in combined adenoma and carcinoma of the

pancreas and 50 mg/kg bw/day in females based on an increase in liver tumours at 500 mg/kg bw/day.

A1.7 Reproductive toxicity

A study on developmental toxicity (Developmental toxicity/teratogenicity) was conducted in rats, according to OECD Guideline 414. Pregnant rats were exposed to FRD-902 (84% purity) at 10, 100, or 1000 mg/kg bw/day by oral gavage during Gestation days 6-20. Dams were sacrificed on Gestation day 21. Organs including the ovaries and uterus, and fetuses were examined.

One female in the highest dose group died on GD 20, due to liver and kidney damage. Four and 9 females in the 100 and 1000 mg/kg/day groups, respectively, delivered early on gestation day 21. The mortality in the 1000 mg/kg/day group and early deliveries in the 100 and 1000 mg/kg/day groups were considered test substance-related. Test-substance related clinical findings (yellow material on various body surfaces, salivation), higher mean kidney weight, and reduction in maternal body weight gains occurred only in the highest dose group. Decreased gravid uterine weights were found in the 100 and 1000 mg/kg/day groups. Increased liver weight was found in the 100 and 1000 mg/kg/day groups and was considered in the report to be related to PPAR α activation. In addition, focal necrosis was observed in the liver of some animals at these dose levels and hepatocellular hypertrophy at the highest dose level. Mean fetal weight was reduced by 8.8% in the 100 mg/kg/day group and by 28.1% in the 1000 mg/kg/day group. No effects were found on fetal survival, on malformations or on variations, except a higher incidence of 14th rudimentary ribs in the highest dose group which was not considered adverse by the registrant.

The increase in early delivery was confirmed in a second study at 1000 mg/kg bw/day in which 3 early deliveries were observed in an unknown number of dams versus none in the controls. The fetal weight was decreased. In addition, comparable maternal effects were observed as in the main study.

The no-observed-adverse-effect level (NOAEL) for maternal toxicity was considered to be 10 mg/kg/day, based on mortality and lower mean body weight gains and food consumption at 1000 mg/kg/day and early deliveries, and microscopic findings in the liver (focal necrosis) at 100 and 1000 mg/kg/day.

The no-observed-adverse-effect level (NOAEL) for developmental toxicity was considered to be 10 mg/kg/day, based on early deliveries and lower mean fetal weights at 100 and 1000 mg/kg/day.

In a one-generation study (OECD TG 421) in mice (n=25) with exposure by oral gavage at dose levels of 0.1, 0.5 and 5 mg FRD-902/kg bw/day (purity 84%), the F0 males were dosed during study days 0 to 84 (70 days prior to pairing through 1 day prior to euthanasia), for a total of 84 to 85 doses. The females that delivered (with the exception of those females selected for toxicokinetic evaluation) were dosed from study day 56 through the day prior to euthanasia (14 days prior to pairing through lactation day 20) for a total of 53 to 64 doses. The females that

were selected for toxicokinetic evaluation were dosed through the day of euthanasia (lactation day 21) for a total of 54 to 65 doses.

Parental animals: no effect on mortality. In the higher dose groups, an increase in body weight was found with a corresponding increase in food consumption. Increased liver weight in the 0.5 and 5 mg/kg/day dose groups. In the highest dose group, an increase in kidney weight was found (only significant in females). Hypertrophy was found in the liver of males and females in the middle and high dose groups, and in the kidneys of males in the middle and high dose groups. Liver necrosis (focal or single cell) and an increase in the presence of mitotic figures was observed at the highest dose level. An increase in single cell necrosis of the liver was also observed in males at 0.5 mg/kg bw/day.

There was no effect on reproductive performance. Mean numbers of F1 pups born, live litter size, percentage of males at birth, postnatal survival, and the general physical condition of the F1 pups were unaffected by test substance administration at all dosage levels. F1 survival was unaffected by test substance administration at all dosage levels following weaning. At the highest dose level, a reduction in body weight gain was observed in male pups, and in female pups only during the pre-weaning period. Minimal delays in sexual maturation were observed, but were related to the reduction in body weight. For both maternal animals and their offspring, male and female mice behaved in a kinetically similar manner, with an approximately linear relationship between dose and blood levels of the test substance. The plasma level in pups on post-natal day (PND) 4 were 2-4 fold below the maternal levels and on PND 21, 40-60 fold lower. On PND 40, after direct gavage exposure of the F1, the plasma levels were comparable between the dams and offspring. Based on these results, the no-observed-adverse-effect level (NOAEL) for reproductive toxicity was 5 mg/kg/day, as no effects on reproduction were observed at any of the doses levels tested. The results indicate limited transfer of FRD-902 via lactation. The NOAEL for systemic toxicity in parental animals was 0.1 mg/kg/day based on the low incidences of single cell necrosis observed in the liver of males at 0.5 mg/kg/day. The NOAEL for systemic toxicity in the offspring was 0.5 mg/kg/day based on body weight decrements in the F1 males and females in the 5 mg/kg/day group during the pre-weaning period.

A1.8 Specific target organ toxicity – repeated exposure

Mice

In a range-finding study not performed according to OECD and GLP, male mice (n=5) were exposed to FRD-902 (86.6% purity) by gavage (water) at 30 mg/kg bw/day. Body (105%) and liver weight (200%) were increased. Histopathology showed an increase in liver hypotrophy, single cell necrosis and mitotic figures (Exp Supporting Repeated dose toxicity:oral.006).

In a 28-day study according to OECD TG 407, groups of 10 or 20 Crl:CD-1(ICR) mice per dose and sex were exposed to FRD-902 (88% purity) by gavage (water) at dose levels of 0.1, 3 and 30 mg/kg bw/day. The reversibility of the effects in the high dose mice was determined after a 4-week recovery period (Exp Supporting Repeated dose toxicity:oral.003).

Body weights were significantly higher compared to controls in the 30 mg/kg/day group males and females at the end of the dosing period. Body weight gain slowed during the recovery period and body weights in the 30 mg/kg/day animals were comparable to the control group by the end of the study. Statistically significant, test substance-related decreases in red cell mass parameters (red blood cells, hemoglobin and/or hematocrit) were present in the 3 and 30 mg/kg/day group males. The changes in red cell mass parameters were minimal (decreased less than 10% compared to controls). Test substance-related serum chemistry findings included changes in liver enzymes and serum proteins in males and females administered 3 or 30 mg/kg/day. Liver enzyme levels (alanine aminotransferase, alkaline phosphatase and sorbitol dehydrogenase) were higher in the 3 and 30 mg/kg/day group males and 30 mg/kg/day group females at study week 4. Aspartate aminotransferase levels were also higher in the 3 and 30 mg/kg/day group males at study week 4. These liver enzyme level changes were consistent with hepatocellular injury, and single cell necrosis was noted microscopically in some animals in these groups. Liver enzyme changes were reversible in both males and females, as levels for all liver enzymes were similar to controls following 4 weeks of recovery. Minimal changes of higher albumin, lower globulin, and associated changes of increased total protein and increased albumin/globulin ratio were present in the 30 mg/kg/day group males. Decreased globulin and increased albumin/globulin ratio were also present in the 3 mg/kg/day group males. A similar pattern of change in serum proteins was present in females administered 3 or 30 mg/kg/day. These serum protein changes were reversible, as there were no statistically significant changes in these parameters in males or females by study week 8. Blood urea nitrogen was slightly increased in the 30 mg/kg/day group males at the end of exposure. Blood urea nitrogen was similar to control values following the 4-week recovery period. The slight increase in urea nitrogen in 30 mg/kg/day group males was not associated with changes in related clinical chemistry parameters or with test substance-related microscopic findings in the kidney. A statistically significant decrease in cholesterol was present in the 3 mg/kg/day group males. This decrease was not dose-related, as mean cholesterol in the 30 mg/kg/day group males was not statistically different from controls and was higher than that of the 3 mg/kg/day group males. However, several individual cholesterol values in treated male groups were below the study control range, and thus, a test substance-related effect of decreased cholesterol cannot be ruled out. However, individual cholesterol values in treated groups were within the testing laboratory historical control values (with the exception of one male in the 3 mg/kg/day group).

Test substance-related gross necropsy findings included enlarged liver in the 30 mg/kg/day group males at the primary necropsy. There were no test substance-related gross necropsy findings at the recovery necropsy. Liver weights were increased in the 3 and 30 mg/kg/day group males and females at the end of the exposure period. These changes correlated with hepatocellular hypertrophy microscopically and with increases in beta-oxidation. Liver weights were mostly, but not completely, reversible in the 30 mg/kg/day males and females. At this dose, liver weight relative to body weight in the 30 mg/kg/day group males was increased by 163.1% above controls at the end of exposure,

and was reduced to 21.5% of control after the 4-week recovery period. Similarly, in 30 mg/kg/day group females, liver weight relative to body weight was increased by 102.7% above controls at the end of exposure and was reduced to 14.3% of control after the 4-week recovery period. Adrenal gland weights (absolute and relative to body and brain weights) were increased in the 3 and 30 mg/kg/day group males at the end of the exposure period. In the 30 mg/kg/day group males, these adrenal weight changes correlated with minimal adrenal cortical hypertrophy microscopically. Adrenal weight changes were reversible following the 4-week recovery period. Decreased uterus weights (absolute and relative to body and brain weights) were present in the 30 mg/kg/day group females at the end of the exposure period. There were no histopathological changes in the uterus that were correlative to the uterine weight changes. Minimal adrenal cortical hypertrophy was observed microscopically in the 30 mg/kg/day group males at the primary necropsy. This change correlated with increased adrenal weights in this group. Adrenal cortical hypertrophy was not observed in the 30 mg/kg/day group males at the recovery necropsy.

Hepatocellular hypertrophy was observed in the 3 and 30 mg/kg/day group males and females at the primary necropsy. This change was consistent with increased liver weights noted in these groups. The hepatocellular hypertrophy was characterized by expansion of the hepatocellular cytoplasm by numerous fine eosinophilic granules. Other findings in the liver included multifocal single cell hepatocellular necrosis in the 3 and 30 mg/kg/day group males and 30 mg/kg/day group females at the primary necropsy, and increased mitoses distributed multifocally throughout the liver section in the 30 mg/kg/day group males and females at the primary necropsy. Incidences of these changes were higher in the males compared to the females. Hepatocellular hypertrophy, single cell hepatocellular necrosis and increased mitoses in the liver were not observed in the 30 mg/kg/day group males and females at the recovery necropsy.

There was an increased number of animals in the diestrus stage of the estrous cycle in the 30 mg/kg/day group females compared to control group females at the primary necropsy. However, ovarian morphology, including number and maturational stages of corpora lutea were similar between treated and control groups, suggesting normal estrous cycling. The significance of the differences in estrous stage distribution between the 30 mg/kg/day group females and control group females is uncertain. The number of animals in the diestrus stage of the estrous cycle was equal in the control and 30 mg/kg/day group females at the recovery necropsy.

The test substance was an inducer of hepatic peroxisomal beta-oxidation activity, a measure of peroxisome proliferation, in male mice after administration of 0.1, 3 and 30 mg/kg/day and in female mice after administration of 3 and 30 mg/kg/day for 28 days. Total hepatic microsomal cytochrome P-450 enzyme content was decreased at a dosage of 3 and 30 mg/kg/day in male mice but not in females. Beta-oxidation activity in both male and female mice had returned to control levels after approximately 28 days of recovery, while total cytochrome P-450 content remained below control levels in the males.

The NOAEL in this study was 0.1 mg/kg bw/day based on several effects mainly in males including liver single cell necrosis, reduction in red blood cell parameters, increased liver weights, hepatocellular hypertrophy, and changes in albumin/globulin ratio at 3 mg/kg bw/day.

In a 90-day study according to OECD TG 408, groups of 10 Crl:CD-1(ICR) mice per dose and sex were exposed to FRD-902 (84% purity) by gavage (water) at dose levels of 0.1, 0.5 and 5 mg/kg bw/day. Additional animals were exposed for evaluation of the plasma concentration of the substance at 2 hours after exposure on day 0, 28 and 95 (Exp Supporting Repeated dose toxicity:oral.007).

There were no test substance-related clinical observations or deaths. No adverse, test substance-related effects on mean body weight or mean body weight gain were observed in any female group. Statistically significant increases in mean final body weight (test day 91) and overall body weight gain (test days 0-91) were observed in the male 5 mg/kg/day group, relative to control. Mean final body weight and overall body weight gain were 108% and 136% of control, respectively. The difference in body weight and body weight gain in the high dose males was attributed primarily to increased liver weight. No adverse, test substance-related effects on mean food consumption or food efficiency were observed in any female group. Statistically significant increases in mean overall (test days 0-91) food consumption and food efficiency were observed in the male 5 mg/kg/day group, relative to control. Mean overall food consumption and food efficiency were 111% and 127% of control, respectively. The higher food efficiency is likely due to increased body weight due to enlarged livers in this group. No ophthalmological signs were observed in any mouse in any group. There were no adverse or treatment-related changes in group mean hematology parameters at test day 96 (males) or 97 (females). Test substance-related increases in a number of liver-related clinical chemistry parameters were present in male and female mice administered 5 mg/kg/day (see Table A5). Increases were mild to severe, were consistently more severe in males compared to females, and included increases in aspartate aminotransferase (AST), alanine aminotransferase (ALT), sorbitol dehydrogenase (SDH), alkaline phosphatase (ALKP) and total bile acids (TBA). Changes in these parameters were consistent with hepatocellular damage and/or cholestasis, correlated microscopically with hepatocellular single cell necrosis in male (10/10) and female (1/10) mice at this dose, and thus were considered to be adverse effects. Total protein (TP) and albumin (ALB) were minimally increased in male mice dosed with 5 mg/kg (110% and 114% of control, respectively). ALB was also minimally increased in female mice at the same dose (104% of control). These changes were considered to be treatment-related due to the consistency of change among individual animals. However, minimally increased total protein and albumin have no toxicological significance; therefore, these changes were considered to be non-adverse by the registrant. Cholesterol (CHOL) was mildly decreased in male mice dosed with 5 mg/kg (74% of control). There are no known adverse effects associated with minimal decreases in cholesterol. Therefore, these changes were considered test substance related but non-adverse by the registrant. Potassium (K) was decreased in male and female mice dosed with 5 mg/kg (87% and 91% of control,

respectively). Decreased K typically occurs when there is a shift of K from extra cellular fluid to intracellular fluid (e.g., in metabolic alkalosis), a decreased dietary intake of K, or an increased loss of K via kidneys (e.g., polyuria), alimentary tract (e.g., diarrhea) or skin (e.g., sweating). In the present study, the relationship of this finding to test substance administration is uncertain. However, there were no clinical signs suggestive of hypokalemia and no test substance-related alterations in sodium (Na). Therefore, the minimal change in K was not considered to be adverse. Chloride (CL) was slightly higher (102% of control) in male mice dosed with 5 mg/kg. Based on the minimal nature of the change and lack of any correlative findings, this change was considered to be unrelated to treatment and non-adverse by the registrant. Under the conditions of the study, the test substance had no effect on neurobehavioral parameters in either males or females.

Organ weights

A test substance related increase in mean liver weight parameters was observed in mice exposed to ≥ 0.5 mg/kg/day in males and 5 mg/kg/day in females (see Table A6). In the 5 mg/kg/day males, mean absolute and mean relative (% brain weight and % body weight) liver weights were increased to 263%, 242%, and 230% of control, respectively. These increases were statistically significant. In the 0.5 mg/kg/day males, mean absolute and mean relative (% brain weight and % body weight) liver weights were also increased (not statistically significant) to 112%, 113%, and 111% of control, respectively. In 5 mg/kg/day females, mean absolute and mean relative (% brain weight and % body weight) liver weights were increased (statistically significant) to 169%, 167% and 169% of control, respectively. Increased liver weight parameters were considered test substance related in males given ≥ 0.5 mg/kg/day and in females given 5 mg/kg/day. The increase in liver weight parameters in both sexes correlated with a treatment-related increase in enlarged liver and microscopic hepatic changes.

Mean relative (to brain) weight of kidneys was increased (statistically significant) in male mice given 5 mg/kg/day of test substance as compared to controls. Although minimal renal tubular hypertrophy was present in this group, the change in kidney weight relative to brain weight was not associated with changes in mean absolute or relative (% body weight) kidney weights. Mean weights of brain and epididymides relative to body weight were lower, and mean weight of heart relative to brain weight was higher in male mice given 5 mg/kg/day of test substance as compared to controls (all statistically significant). These changes occurred without correlative changes in other weight parameters for these organs or with microscopic findings.

Gross pathology

At the terminal sacrifice, enlarged and/ or discolored livers were observed in 4/10 and 9/10 male mice exposed to 0.5 mg/kg/day and 5 mg/kg/day of test substance respectively. In the 5 mg/kg/day group 3/10 female mice had enlarged livers (see Table A7). These gross changes were considered test substance related. Liver enlargement and discoloration correlated with test substance related increases in liver

weights and microscopic hepatocellular hypertrophy.

Histopathology: non-neoplastic

Test substance related and adverse microscopic findings were present in the liver of male and female mice administered 5 mg/kg/day of the test substance (see Table A8). At 0.5 mg/kg/day, test substance related microscopic changes were limited to male mice which had minimal hepatocellular hypertrophy, without evidence of liver cell injury. In the 5 mg/kg/day male and female groups, test substance-related hepatocellular hypertrophy was present in all animals. Hypertrophy was graded as mild (grade 2 out of 4) in males and minimal (grade 1 out of 4) or mild in females. The distribution of the hepatocellular hypertrophy was centrilobular when of minimal severity and diffuse when of mild severity. Hypertrophy was morphologically consistent with peroxisome proliferation and was characterized by increase in the size of hepatocytes due to increased amount of finely granular eosinophilic cytoplasm and enlarged nuclei with occasional binucleated cells. Additional liver changes in the 5 mg/kg/day group occurred most consistently in males and included increased numbers of mitotic figures (males only), increased pigment (likely lipofuchsin) in Kupffer cells, and single cell hepatocellular necrosis. The latter change was characterized by isolated eosinophilic bodies with occasional pyknotic nuclear fragments and unaccompanied by inflammation, and thus was consistent with apoptosis. Hepatic lesions correlated with increased absolute and relative liver weight and increased total bile acid and liver enzyme levels (AST, ALT, SDH, ALP). Minimal bile duct hyperplasia was present in the liver of one male mouse in the 5 mg/kg/day group. Since similar changes were not seen in any other treated mice, the relationship of this finding to test substance administration is uncertain. In the 0.5 mg/kg/day groups, liver changes were limited to minimal hepatocellular hypertrophy in males only. In females, focal necrosis was present in both treated and control mice with slightly increased incidence in the 5 mg/kg/day females (1/10, 0/10, 2/10, 3/10 in control, 0.1, 0.5, and 5 mg/kg/day groups, respectively). Focal hepatic necrosis is a common background lesion in mice, and there was no difference in morphology or severity of this lesion in treated female mice as compared to controls. In addition, test substance-related focal necrosis did not occur in males, the more sensitive gender for liver effects. Therefore, the minimal increase in the incidence of this lesion in high dose females was considered spurious and unrelated to treatment.

Test substance related changes in the kidney were limited to minimal tubular epithelial hypertrophy in 9/10 male mice given 5 mg/kg/day of the test substance. Hypertrophy was characterized by slightly enlarged epithelial cells containing increased amounts of fine granular eosinophilic cytoplasm. Tubular epithelial hypertrophy was not associated with renal tubular cell degeneration/necrosis. Also there was no change in clinical pathology parameters indicative of renal injury.

Plasma Concentration Evaluation

The test substance concentration in blood was almost similar on days 0, 28, and 95 in female mice, indicating that steady-state concentrations were almost achieved on the first day of dosing. This is consistent with a test substance that was cleared rapidly from the blood within one dosing

interval. The test substance concentration in blood from male mice was lower on day 0 than on day 28, and for the high dose the concentrations on day 28 were slightly lower than day 95 concentrations, indicating steady state may not have been achieved by day 28. Compared to female mice, male mice took longer to achieve steady-state concentrations in blood. The plasma concentration was linear with dose, implying that absorption was not saturated over the range of doses tested in this study. Test substance was not present in plasma from control animals.

Table A5. Clinical chemistry.

	Male Mice – Test Day 96				Female Mice – Test Day 97			
Dosage (mg/kg)	0	0.1	0.5	5	0	0.1	0.5	5
AST (U/L)	62	67 ^a	84	128	68	71	69	74
		108% ^b	135%	206%		104%	101%	109%
ALT (U/L)	49	62	66	255	36	36	32	51
		127%	135%	520%		100%	89%	142%
SDH (U/L)	26.6	26.0	25.8	108.5	25.3	22.9	23.6	33.5
		98%	97%	408%		118%	111%	243%
ALKP (U/L)	50	55	70	617	65	77	72	158
		110%	140%	1234%		118%	111%	243%
TBA (μmol/L)	1.2	1.2	1.4	11.1	4.3	2.3	2.7	13.2
		100%	117%	925%		53%	63%	307%

^a – mean, ^b – % of control, **bold** = statistically significant

Table A6. Test Substance-Related Effects on Mean Absolute and Relative Liver Weights.

Dose (mg/kg/day)	0	0.1	0.5	5
Male				
Number of mice	10	10	10	10
Mean final body weight (grams)	38.7	40.3	38.9	44.3*
Liver				
absolute weight (grams)	1.955	2.024	2.186	5.144*
Liver weight/body weight x 100	5.06	5.028	5.618	11.637*
Female				
Number of mice	10	10	9	9
Mean final body weight (grams)	32.2	32.1	32.6	32.4
Liver				
absolute weight (grams)	1.693	1.697	1.745	2.867*
Liver weight/body weight x 100	5.225	5.309	5.337	8.811*

* Statistically significant as compared to control value.

Bold values were interpreted to be test-substance related increases, as compared to control values.

Table A7. Test Substance-Related Gross Observations in Mice.

	Male				Female			
Dose (mg/kg/day)	0	0.1	0.5	5	0	0.1	0.5	5
mice/group:	10	10	10	10	10	10	10	10
Liver	(10)	(10)	(10)	(10)	(10)	(10)	(10)	(10)
Large	0	0	1	9	0	0	0	3
Discoloration	0	0	4	5	1	0	0	3

Numbers in parentheses are the number of tissues examined within each group.
Bold values were interpreted to be test substance-related gross findings.

Table A8. Incidences of Test Substance-Related Microscopic Findings in the Liver of Male and Female Mice.

	Male				Female			
Dose (mg/kg/day)	0	0.1	0.5	5	0	0.1	0.5	5
mice/group	10	10	10	10	10	10	10	10
Liver	(10)	(10)	(10)	(10)	(10)	(10)	(10)	(10)
Hepatocellular hypertrophy	0	0	8	10	0	0	0	10
Hepatocellular single cell necrosis	0	0	0	10	0	0	0	1
Mitotic figures	0	0	0	9	0	0	0	0
Pigment increased, Kupffer cells	0	0	0	10	0	0	0	2

Numbers in parentheses are the number of tissues examined within each group.
Bold values were interpreted to be test substance-related gross findings.

RIVM opinion: Several statistically significant effects observed in this study were considered substance related but not adverse by the registrant because of the small effect size. We agree that not all statistically significant effects are also biologically significant. In addition, a minimal effect size is applied in the Bench Mark Dose approach to derive limit values. However, for some of the effects in the current study, the justification for the absence of adversity based on the effect size is too limited and not accepted. The NOAEL in this study is 0.1 mg/kg bw/day based on an increase in liver weight and hypertrophy observed at 0.5 mg/kg bw/day. According to the EFSA opinion on PFOA (EFSA, 2008) "These changes [liver] are often classified as adaptive and reversible. However, as these represent biological changes possibly related to effects such as tumour promotion and/or changes in drug-metabolizing enzyme activities, [...] the findings should be critically evaluated." In addition, the reversibility is of less relevance for substances with potential continues and lifelong exposure.

Rats

In a screening study not according to OECD and GLP, 5 CrI:CD(SD) rats per dose and sex were exposed by gavage (water) to FRD-902 (86.6% purity) for 7 days to 30, 300 and 1000 mg/kg bw/day (Exp Supporting Repeated dose toxicity:oral.004). Additional animals at 30 mg/kg bw/day were used to collect toxicokinetic information which was not reported in the robust study summary.

Effects on body weight was significant at the high dose level in male rats, 92.4% of control \pm 2.0%. Statistically significant decreases in red cell mass parameters (red blood cell, hemoglobin and hematocrit) were observed in male rats at 300 and 1000 mg/kg/day and in females at 1000 mg/kg/day. Statistically significant increases in red cell distribution width, reticulocytes and neutrophils were also present in 1000 mg/kg/day females. Decreases in serum lipids (triglycerides and/or cholesterol) and globulins were present in all dosed male groups and in females at 300 and/or 1000 mg/kg/day. Other changes in clinical chemistry parameters occurred at 300 and/or 1000 mg/kg/day and included increased alanine aminotransferase (ALT), aspartate aminotransferase (AST), urea nitrogen (BUN), and Glucose; and decreased sorbitol dehydrogenase (SDH), creatinine, and calcium.

Increased liver weight parameters were present in males at all dose levels and in females in the 1000 mg/kg/day group. These liver weight changes were correlative to microscopic hepatocellular hypertrophy in the liver. Other organ weight changes included decreases in heart weight parameters (1000 mg/kg/day males) and increases in some kidney weight parameters (1000 mg/kg/day females). There were no correlative microscopic changes in these organs. Test substance-related microscopic changes were limited to hepatocellular hypertrophy in the liver. Minimal to mild hypertrophy was present in male rats at all doses and in females administered 1000 mg/kg/day. Microscopic and organ weight changes in the liver were associated with increases in beta-oxidation and/or increases in total cytochrome P-450 enzyme activity.

A statistically significant increase in peroxisomal beta-oxidation activity was present in the 30, 300, and 1000 mg/kg/day male groups and in the 1000 mg/kg/day female group at the 7-day sacrifice. A statistically significant increase in total microsomal cytochrome P-450 content was present in the 300 and 1000 mg/kg/day male groups and in the 1000 mg/kg/day female group at the 7-day sacrifice.

In a 28-day repeated dose toxicity study according to OECD 407, groups of 10 CrI:CD(SD) rats per dose and sex were exposed to FRD-902 (purity 88%) by gavage (water). Males were exposed to 0.3, 3 and 30 mg/kg bw/day whereas females were exposed to 3, 30 and 300 mg/kg bw/day. Additional animals were used to determine the recovery within 4-weeks (Exp Supporting Repeated dose toxicity:oral.001).

All animals survived to the scheduled necropsies. Yellow material around the urogenital area was noted occasionally for 9 females in the 300 mg/kg/day group at 1 to 2 hours post-dosing from study day 3 to 25. This finding was not noted during the recovery period. There were no test substance-related effects on body weight. Minimal, statistically

significant decreases in red cell mass parameters (RBC, hemoglobin and hematocrit) were present in the 3 and 30 mg/kg/day male groups. These decreases were associated with minimal increases in absolute reticulocyte counts. The decreases in red cell mass parameters were minimal ($\leq 7.9\%$ below the control mean for all parameters), and values for red cell mass parameters and reticulocyte counts in individual animals in the 3 and 30 mg/kg/day male groups were within the testing laboratory historical control ranges for the respective parameters. There were no statistically significant changes in red cell mass parameters or reticulocytes following the 4-week recovery period. Test substance-related and statistically significant decreases in cholesterol were present in all treated male groups. Decreases were minimal (not reported), as values for most animals were within or only slightly below the testing laboratory historical control range. Based on the minimal nature of the changes, as well as the direction of change (decreased rather than increased), these changes in cholesterol were not considered to be adverse by the registrant. However, as the effect size is unknown this conclusion is not agreed by the RIVM. Comparable reductions were observed in other studies and can be related to the increased beta-oxidation. Effects on cholesterol were reversible as cholesterol values were actually increased compared to controls following the approximately 4-week recovery period, although cholesterol values for all animals in the 30 mg/kg/day recovery group were within the testing laboratory historical control range. Higher albumin and lower globulin levels, as well as associated increases in albumin/globulin ratio, were present in the 3 and 30 mg/kg/day male groups. Increased albumin and albumin/globulin ratio were also present in the 300 mg/kg/day female group. Changes in globulin were minimal (not reported), as individual values for all animals in the 3 and 30 mg/kg/day male groups were within the testing laboratory historical control range, with the exception of one rat in the 30 mg/kg/day group whose value was just below the testing laboratory historical control range. Similarly, increases in albumin in the affected male and female groups were within the testing laboratory historical control range, or, for some animals in the 30 mg/kg/day male group, were only slightly above the testing laboratory historical control range. The changes in serum proteins were considered to be test substance related. However, these changes were not considered to be adverse based on their minimal nature at all dose levels by the registrant. In addition, all serum protein changes were reversible, as mean values were similar to controls following the 4-week recovery period. Urea nitrogen was minimally increased in the 30 mg/kg/day group males. This increase was not associated with changes in creatinine or with treatment-related microscopic changes in the kidney. The minimal increase in urea nitrogen is likely of non-renal origin. The pattern of changes in urea nitrogen, as well as those noted above for serum proteins, is consistent with those reported for other peroxisome proliferators. Changes in urea nitrogen were reversible in males, as there were no statistically significant changes in these parameters following the recovery period. Glucose levels were minimally increased (15.2% higher than the control group mean) in the 30 mg/kg/day group males at study week 4, but were lower than the control group at study week 8. These increases were within the testing laboratory historical control ranges and were not considered adverse. Mean triglyceride values in treated male groups were lower than

controls. These decreases did not occur in a dose-related manner and were statistically significant only in the 3 mg/kg/day group. The group means for the treated groups were actually similar to the historical control mean, while the concurrent study control group mean of 72 mg/dL was higher than the mean of the historical control data, which was 48 mg/dL. Individual triglyceride values in animals from all treated male groups were within the testing laboratory historical control range. While some peroxisome proliferators have been shown to lower triglycerides in rodents, it is unclear if the triglyceride effects in the current study are test substance-related. The effects are not considered to be adverse by the registrant, as changes were minimal and individual triglyceride values in treated groups were similar to those seen normally in this species and strain. There were no significant elevations in group mean liver enzyme values in test substance-treated males and females.

Significantly higher liver weights occurred in a dose-related manner in males administered 3 or 30 mg/kg/day group and in females in the 300 mg/kg/day group. These findings correlated with histologic evidence of centrilobular hypertrophy. Following the recovery period, the absolute liver weight and organ-to-body-weight ratios of males from the 30 mg/kg/day group and females from the 300 mg/kg/day group did not significantly differ from the control group values. There were no other test substance-related effects on organ weights. However, some statistically significant differences were observed when the control and test substance-treated groups were compared. The absolute kidney weight was higher for the 3 and 30 mg/kg/day group males relative to the control group and kidney weights relative to body or brain weight were higher for the 30 mg/kg/day group males relative to the control group. These differences were small in magnitude and lacked a morphologic or clinical pathology correlate. Therefore, the kidney weight effects were not considered to be adverse according to the registrant.

Test substance-related changes of multifocal centrilobular hypertrophy were observed in the liver of 3 and 30 mg/kg/day group males and the 300 mg/kg/day group females. The tissue alteration was characterized by enlargement of hepatocytes surrounding central veins. Changes, graded minimal and mild, were diagnosed as a relative change when compared to periportal hepatocytes. Although females were administered higher doses of test substance, changes were more subtle than in males. Histologic examination of the liver from recovery animals revealed no evidence of centrilobular hypertrophy.

In male rats, beta-oxidation activity was statistically significantly increased at the 28-day time point at all dosage levels. At 0.3 mg/kg/day the increase was minimal (about 1.4-fold higher than control), with more moderate increases of about 3.7- and 8.7-fold above control in the 3 and 30 mg/kg/day male groups, respectively. In female rats dosed with 30 and 300 mg/kg/day test substance, beta-oxidation activity was statistically significantly increased (about 1.5- and 3.0-fold higher than controls, respectively) at the 28-day time point. Beta-oxidation activity had returned to control levels after approximately 28 days of recovery in both male and female rats. A minimal, statistically significant increase in total cytochrome P-450 was present in the 30 mg/kg/day male group at the 28-day time point, but had returned to

control levels after approximately 28-days recovery. There were no effects on total cytochrome P-450 content in female rats.

No NOAEL could be derived from this study because at the lowest dose of 0.3 mg/kg bw/day in males, a decrease in cholesterol levels was observed. The level of decrease is unknown. However, reductions in cholesterol were also observed in other studies and could be related to the increase in beta-oxidation. Therefore, currently this effect cannot be discounted as non-adverse. In addition, an increase in beta-oxidation of 1.4 times the control level was determined. This effect at such low level of increase is not considered adverse. If the additional details of the study report provide sufficient justification to conclude that the decrease in cholesterol is not adverse, a NOAEL of 0.3 mg/kg bw/day can be derived from this study.

In a 90-day repeated dose toxicity study according to OECD 408, groups of 10 Crl:CD(SD) rats per dose and sex were exposed to FRD-902 (purity 84%) by gavage (water). Males were exposed to 0.1, 10 and 100 mg/kg bw/day whereas females were exposed to 10, 100 and 1000 mg/kg bw/day. Additional animals were used to determine the recovery within 4-weeks (Exp Supporting Repeated dose toxicity:oral.002).

There were 2 test-substance-related deaths and 1 death of uncertain relationship to test substance administration in the 1000 mg/kg/day group females. Female no. 7323 was euthanized in extremis on study day 8 with clinical observations of impaired use of the hindlimbs and forelimbs. Female nos. 7315 and 7318 were found dead on study days 21 and 37, respectively. All 3 females were noted with clear material around the mouth and/or yellow material on various body surfaces at approximately 1-2 hours post-dosing on study days 7 and 8 (no. 7323) or intermittently from study days 0 to 20 (no. 7315) and 27 to 36 (no. 7318). At necropsy, the female euthanized in extremis (no. 7323) had gross lesions of red areas in the stomach, urinary bladder, and thymus and microscopically observed necrosis, hemorrhage, and thrombus of the spinal cord, thrombosis, myocardial fiber degeneration, and necrosis in the heart, necrosis of the glandular stomach, and hemorrhage in the lung, thymus, and urinary bladder. The first female found dead (no. 7315) had renal tubular and papillary necrosis, hepatocellular hypertrophy, and lymphoid depletion in multiple tissues. The second female found dead (no. 7318) had renal papillary necrosis and necrosis of portions of an adrenal gland, hyperplasia of the transitional epithelium of the urinary bladder, hepatocellular hypertrophy, and lymphoid depletion in multiple tissues. The early death of female nos. 7315 and 7318 was considered to be test substance-related because both females shared similar microscopic findings (renal papillary necrosis, hepatocellular hypertrophy, and lymphoid depletion in multiple tissues). The other early death female (no. 7323) in this group died earlier (study day 8) than the unscheduled death female nos. 7315 and 7318 (study days 21 and 37, respectively) and had microscopic findings that were not observed in the other animals in this group. Thus, the relationship of this early death of female no. 7323 to treatment was uncertain.

There were no adverse clinical observations or effects on survival for any test substance-treated male groups and for the 10 and 100

mg/kg/day group females. Clinical observations in the 1000 mg/kg/day group females were noted in at least half of the surviving females and included clear material around the mouth, neck, and/or forelimb(s), yellow material on various body surfaces (at time of dosing and approximately 1-2 hours post-dosing) and red material on various body surfaces (1-2 hours post-dosing) beginning on the third day of dosing for some females.

There were no test substance-related effects on body weight at any dosage level. Mean body weights for the high-dose group males (100 mg/kg/day) and females (1000 mg/kg/day) were approximately 97% and 102% of the control group mean value, respectively (neither statistically significant). Mean overall food consumption during the dosing period for the high-dose group males (100 mg/kg/day) and females (1000 mg/kg/day) were 100% and 111% of the control group value, respectively (statistically significant in females). In males, significantly lower mean food consumption was recorded for study week 0 to 1 for the 10 and 100 mg/kg/day group, and from study week 1 to 2 for the 100 mg/kg/day group.

No ophthalmic lesions indicative of toxicity were observed in any of the test substance-treated groups.

Test substance-related hematology changes in red cell mass parameters (red blood cell counts, hemoglobin, and hematocrit) were present in the high-dose group males (100 mg/kg/day) and females (1000 mg/kg/day) at the end of the dosing period. These parameters were approximately 11%-13% lower in males and 18%-28% lower in females when compared to the respective control group. In addition, individual values for these erythrocyte parameters in several animals at these dose levels were below historical control reference ranges. The lower red cell mass parameters were associated with higher absolute reticulocyte counts in both sexes, and in females, were associated with changes in red cell parameters, including higher mean corpuscular volume (MCV) and mean corpuscular hemoglobin (MCH), and lower mean corpuscular hemoglobin concentration (MCHC). The changes in reticulocyte counts and red cell parameters indicated a regenerative response to the lower red cell mass. Consistent with their regenerative nature, the red cell changes in the high-dose group males and females showed recovery following the approximate 4-week recovery period. In females, recovery was complete as values for some red cell mass parameters were statistically higher (along with lower reticulocytes and an equivocal higher MCV) when compared to the control group. In males, recovery was present but was not complete as slightly lower (about 5% below the control group) red cell mass parameters were still present at the end of the recovery period when compared to the control group. In addition, absolute reticulocyte counts remained minimally elevated in this group. Based on the regenerative response noted in the high-dose group males at the recovery evaluation, complete recovery would be expected with increased recovery time. Statistically significant lower erythrocyte parameters were also present in the 10 mg/kg/day group males when compared to the control group. At this dose level, the magnitude of changes were minimal (approximately 7% below the control group), and values for individual animals were within historical control reference

ranges (except for the hematocrit values in 2 males which were 0.2 percentage points below the reference range). Consistent with the minimal nature of the erythrocyte changes at this dose, there were no statistically significant changes in absolute reticulocyte counts. Based on the minimal nature of the effects on red cell parameters, the lack of an increase in reticulocyte counts suggesting a lack of an erythropoietic stimulus, and the absence of anemia in individual animals, the erythrocyte effects in the 10 mg/kg/day male group were not considered to be adverse by the registrant. Some other statistically significant differences in hematology parameters were noted when the control and test substance-treated groups were compared. These findings included lower activated partial thromboplastin time (APTT) at the recovery (study week 17) evaluation for the 100 mg/kg/day group males and lower absolute basophil counts at study week 13 for the 100 mg/kg/day group males. These group mean differences were not considered test substance-related because according to the registrant they did not occur in a time-related manner or they were not of a magnitude that would be considered toxicologically important.

Test substance-related and statistically significant changes in several serum chemistry parameters were present in the 10 and 100 mg/kg/day group males and the 100 and 1000 mg/kg/day group females when compared to the control group. Most changes were consistent with PPAR α activation. Test substance-related lower (variable statistical significance) cholesterol values were present in the 10 and 100 mg/kg/day group males (-31%) and the 100 (-20%) and 1000 mg/kg/day group (-31%) females. The differences from the control group were minimal, as values for most animals in the affected groups were within historical control reference ranges. There are no known adverse effects associated with minimally lower levels in cholesterol according to the registrant. As such, these changes were considered by the registrant to be test substance-related but non-adverse. However, this is questioned by the RIVM. Test substance-related effects on cholesterol values were reversible in both males and females as there were no statistically significant changes in cholesterol values in the high-dose group when compared to the control group following the 4-week recovery period. In addition, there were no test substance-related changes in triglycerides in male or female rats at any of the dosage levels tested. Higher albumin (males only +10% and 12%) and lower globulin levels (both sexes -12% and -15% and -33%), as well as associated higher albumin/globulin ratios (+26% and +35% and +58%), were present in the 10 and 100 mg/kg/day group males and the 1000 mg/kg/day group females when compared to the control group. A lower total protein level (due to lower globulin) was also present in the 1000 mg/kg/day group females (-10%). Individual values for these protein parameters were outside the historical control reference ranges in 2 high-dose group females. All serum protein changes were reversible, as mean values were similar to the control group following the 4-week recovery period. The biological significance of the changes (lower) in total protein levels is uncertain. The pattern of change in serum proteins (lower globulin and higher albumin levels) was consistent with the known anti-inflammatory properties of a PPAR α agonist. The anti-inflammatory response to PPAR α activation is characterized by lower levels of acute phase proteins (which contribute

to the globulin fraction), and higher levels of negative acute phase protein (albumin).

The urea nitrogen level was minimally higher (+38%) in the 100 mg/kg/day group males when compared to the control group. This higher level was likely of non-renal origin, as it was not associated with changes in creatinine, urinalysis parameters, or renal histopathology. As with the serum protein changes, the pattern of changes in urea nitrogen was consistent with those reported for other peroxisome proliferators. Changes in urea nitrogen levels were reversible in males, as there were no statistically significant changes in these parameters when compared to the control group following the approximate 4-week recovery period. Alkaline phosphatase levels were minimally higher in the 10 (+48%) and 100 mg/kg/day group (+106%) males and in the 1000 mg/kg/day group females (+66%) when compared to the control group. Alkaline phosphatase levels may be higher in association with cholestatic liver disease; however, in this study, other markers of cholestatic liver injury were not increased (bilirubin and gamma glutamyltransferase levels were actually lower in the 1000 mg/kg/day group females), and there were no effects on other enzymes indicative of hepatocellular injury (alanine aminotransferase, aspartate aminotransferase, and sorbitol dehydrogenase levels). Additionally, there was no histopathological evidence of liver cytotoxicity. Therefore, these minimally higher alkaline phosphatase levels were the result of extra-hepatic factors and were likely due to induction of liver microsomal enzymes. Total bilirubin and gamma glutamyltransferase values were lower in the 1000 mg/kg/day group females when compared to the control group. Total bilirubin was also lower in the 100 mg/kg/day group females. These changes were considered to be test substance-related but non-adverse based on the direction of change (lower rather than higher). The changes in both parameters were reversible following the approximate 4-week recovery period. At study week 17 (recovery evaluation), lower creatinine and higher potassium levels were noted for the 100 mg/kg/day group males when compared to the control group. These group mean differences were not considered to be test substance-related because the values did not show a time-related response, were of a magnitude that would be considered to be toxicologically unimportant, or involved a change in a direction of no known biological importance.

There were no test substance-related effects on urinalysis parameters in the 0.1, 10, and 100 mg/kg/day group males and the 10 and 100 mg/kg/day group females. Test substance-related higher urine volume (statistically significant) and a lower urine osmolality (not statistically significant) suggestive of diuresis were present in the 1000 mg/kg/day group females at study week 13 as compared to the control group. Lower urine pH (statistically significant) was also present in the 1000 mg/kg/day group females at study week 13 as compared to the control group.

There were no significant changes in the functional observation battery.

Test substance-related organ weight changes consisted of higher kidney and liver weights. Higher liver weights in the 10 and 100 mg/kg/day group males and the 1000 mg/kg/day group females correlated with

microscopic hepatocellular hypertrophy, but they were not associated with degeneration or necrosis in the liver or with changes in serum chemistries suggestive of liver toxicity. Therefore, higher liver weights were not considered to be adverse by the registrant. However, this is questioned by the RIVM. In the 100 mg/kg/day group males, liver weight changes were reversible except for liver weight relative to body weight, which was mostly, but not completely reversible. In the 1000 mg/kg/day group females, liver weight changes showed partial recovery, but were not completely reversible following the 4-week recovery period.

All kidney weight parameters (absolute, relative to body and brain weight) were minimally higher in the high-dose group males (100 mg/kg/day) and females (1000 mg/kg/day) when compared to the control group. In the 1000 mg/kg/day group females, these changes were associated with evidence of diuresis (increased urine volume and decreased urine osmolality) and microscopic changes in the kidneys, most commonly in the early death animals. In the 100 mg/kg/day group males, there were no clinical pathology or microscopic changes suggestive of kidney injury. Minimally higher kidney weights were also present in males at the recovery evaluation but not in females. Kidney weight relative to body weight was also higher and statistically significant in the 10 mg/kg/day group males and females and the 100 mg/kg/day group females when compared to the control group. However, at these dosage levels, there were no changes in other kidney weight parameters (absolute and relative to brain weight), and no correlative changes in serum chemistry, urinalysis, or histopathology suggestive of renal toxicity. Thus, higher kidney weights relative to body weight in the 10 mg/kg/day group males and females and the 100 mg/kg/day group females were not considered to be adverse by the registrant.

There were no test substance-related macroscopic findings noted at the scheduled necropsies. Macroscopic findings of uncertain pathogenesis were noted for the 1000 mg/kg/day group female (no. 7323) euthanized in extremis on study day 8 and consisted of red areas in the stomach, urinary bladder, and thymus.

In addition to the microscopic changes observed in the 1000 mg/kg/day group females found dead or euthanized in extremis, one 1000 mg/kg/day group female (animal no. 7279) had minimal renal tubular necrosis and regeneration at the study week 13 primary necropsy.

Minimal hepatocellular hypertrophy was observed in the liver of some males in the 10 and 100 mg/kg/day groups and some females in the 1000 mg/kg/day group at the primary necropsy (see Table A10). Hepatocellular hypertrophy was associated with increased eosinophilic granularity of the hepatocyte cytoplasm consistent with peroxisome proliferation. Hypertrophy was not associated with microscopic changes indicative of liver injury (such as degeneration or necrosis) or with changes in serum chemistry indicative of liver injury, nor was hypertrophy observed in animals at the recovery necropsy.

Table A9. Test Substance-Related Organ Weight Changes.

Parameter	Direction and magnitude of change	Dosage level (mg/kg/day)	Sex	Necropsy
Kidney				
Absolute	↑10.6%*	100	M	Primary
Relative to body weight	↑12.9%*, 16.2%**	10, 100	M	Primary
Relative to brain weight	↑11.6%*	100	M	Primary
Absolute	↑10.8%**	100	M	Recovery
Relative to body weight	↑11.5%**	100	M	Recovery
Relative to brain weight	↑9.4%**	100	M	Recovery
Kidney				
Absolute	↑18.3%**	1000	F	Primary
Relative to body weight	↑9.3%*, 9.5%*, 23%**	10, 100, 1000	F	Primary
Relative to brain weight	↑17.9%**	1000	F	Primary
Liver				
Absolute	↑22.8%*, 59.4%**	10, 100	M	Primary
Relative to body weight	↑30.9%**, 67.0%**	10, 100	M	Primary
Relative to brain weight	↑25.5%**, 61.2%**	10, 100	M	Primary
Relative to body weight	↑10.6%**	100	M	Recovery
Liver				
Absolute	↑77.3%**	1000	F	Primary
Relative to body weight	↑84.6%**	1000	F	Primary
Relative to brain weight	↑76.7%**	1000	F	Primary
Absolute	↑18.5%*	1000	F	Recovery
Relative to body weight	↑14.6%**	1000	F	Recovery
Relative to brain weight	↑17.6%*	1000	F	Recovery
* = Significantly different from the control group at 0.05 using Dunnett's test				
** = Significantly different from the control group at 0.01 using Dunnett's test				

Table A10. Incidence of Hepatocellular Hypertrophy at the Primary Necropsy.

Dosage Level (mg/kg/day)	Males				Females			
	0	0.1	10	100	0	10	100	1000
Liver ^a	10	10	10	10	10	10	10	10
Hepatocellular hypertrophy	0	0	3	10	0	0	0	0
Minimal								

^a = Number of tissues examined from each group.

A NOAEL of 0.1 mg/kg bw/day was derived from this study based on decreased red blood cell parameters, cholesterol and increased A/G ratio, liver weight and hypertrophy and kidney weight at the next higher dose level of 10 mg/kg bw/day.

In a 2-year oral exposure study according to OECD TG 453, rats (n=80) were dosed by gavage with 0.1, 1, or 50 mg/kg bw/day for up to 104 weeks (male rats) or with 1, 50, or 500 mg/kg bw/day for up to 101 weeks (female rats). Interim section was performed on 10 animals per dose and sex after one year (Rae et al, 2015).

Exposure to FRD-902 (purity 84%) did not affect survival. A single test article-related cause of death/moribundity was inflammation/necrosis of the kidneys which occurred in seven of the 500 mg/kg/day females and was characterized by papillary necrosis. In males the most common causes of death/moribundity were pituitary tumours and undetermined. In females the most common causes of death/moribundity were mammary tumour and pituitary tumour. Females were terminated during Week 101, prior to scheduled termination, due to low survival in all female dose groups, especially control and 50 mg/kg/day groups. However, this did not impact the study as this was approximately 2 years of test article exposure. Even though survival among all female groups was low there were no statistically significant differences and survival was comparable among all groups. There were no test article-related clinical observations.

Mean body weight in 50 mg/kg/day males was statistically significantly below control over most of the first year, although mean body weight was only 4% below control in males at Week 52 (not statistically significant), and exceeded the control value at termination. Mean body weight gain in this group was 6% below control in males over Weeks 1 to 52 and exceeded the control value over the two year period. Based on the small magnitude of the changes, the effect among males at 50 mg/kg/day was not considered adverse. Exposure to 500 mg/kg/day of the test substance produced adverse reductions in body weight and body weight gain in females. In this group, statistically significantly lower mean body weight was observed from weeks 30 through 86. Mean body weight was 13% below control at Week 52, and mean body weight gain was 20% below controls over Weeks 1 to 52 (both statistically significant). Mean final body weight (week 100) and overall body weight gain (Weeks 1-100) were comparable to the control value. However, these body weight changes were considered adverse at this dose based on the difference during the first year on study.

There were no adverse test article-related effects on food consumption in either sex or in food efficiency in males at any dose. Adverse effects on food efficiency were observed in 500 mg/kg/day females. In this group, food efficiency was 23% below control (statistically significant) over the first year and 11% below control (statistically significant) overall (Weeks 1-100). Lower mean food efficiency was noted over the first year in males at 50 mg/kg/day. However, overall (Weeks 1-104) food efficiency was comparable to controls. No effects were noted in any other dose group. No test article-related findings were noted in the interim or terminal ophthalmoscopic examination.

At the 3, 6, and 12 month intervals there were mild decreases in red cell mass (erythrocytes, haemoglobin, and hematocrit in females receiving 500 mg/kg/day. Effects were mild in females (up to 28% less than control) and were not associated with any test article-related effects on erythrocyte morphology. Appropriate increases in reticulocytes (106% above respective) occurred in response to the decreases in red cell mass. The increases in reticulocytes were associated with expected decreases in MCHC and increases MCV. This collection of findings is suggestive of red cell loss or haemolysis although the exact mechanisms involved are unknown. Statistically significant decreases in red cell mass were also present in males receiving 50 mg/kg/day at the 3- and 6-month interval. However, the decreases were small (-9 to -7%) and did induce a non-statistically significant increase in reticulocytes. In addition, red mass changes were transient— at the 12 month interval there were no statistically significant changes in any red cell mass parameter, and values in individual animals in the 50 mg/kg/day group were similar to controls. Therefore, the red cell mass changes in 50 mg/kg/day males were considered to be test article-related but non-adverse by the registrant. Bilirubin levels were statistically significant reduced in females at the mid (-21 to -31%) and high dose groups (-33 to -47%) at almost all intervals.

At the 12-month interval in males receiving 50 mg/kg/day, there were mild increases relative to controls in enzymes indicative of liver injury including alkaline phosphatase, ALT, AST and sorbitol dehydrogenase (sorbitol dehydrogenase and AST not statistically significant). These enzyme changes correlated with microscopic findings of minimal cystic degeneration and minimal to mild focal necrosis in the liver of males at 50 mg/kg/day. Therefore, these enzymes changes were considered test article-related and adverse. Minimal but statistically significant increases in alkaline phosphatase were also present at the 3- and 6-month intervals in the 50 mg/kg/day male group. At these intervals, increases in alkaline phosphatase were less than those present at 12 months and were not associated with statistically significant changes in other enzymes indicative of hepatic or hepatobiliary injury. Therefore, the changes in alkaline phosphatase in the 50 mg/kg/day male group at the 3 and 6 month intervals may be due in part or in whole to test article-related enzyme induction, as the test article was previously shown to produce an increase in total P450 enzyme activity in male rats at 30 mg/kg/day. There were no test article-related changes in liver enzymes in males receiving 1 or 0.1 mg/kg/day or in females at any of the dose levels tested (up to 500 mg/kg/day).

Serum Proteins: Minimal, statistically significant increases in albumin were present in males receiving 50 mg/kg/day at all intervals (up to 16% above controls) and in females receiving 500 mg/kg/day at the 3-month interval (10% above controls). In addition, statistically significant decreases (of up to 17% below control) in globulin were present in females at 500 mg/kg/day at all intervals (an associated decrease in total protein was also present in this group at the 6-month interval). No statistically significant decreases in globulin were present in males at any dose or interval except for males at 50 mg/kg bw/day after 3-months, small decreases in individual values for these parameters in individual animals in the 50 mg/kg/day male group may have been test article-related. The changes in albumin and globulin in the high-dose male (+18 to +28%) and female groups (+20 to +23%) also resulted in statistically significant increases in albumin/globulin ratio in these groups at all intervals. The test article is a peroxisome proliferator, and the pattern of change in serum proteins observed in high dose males and females—lower globulin and higher albumin—is a well-established response to PPAR α activation. Peroxisome proliferators are anti-inflammatory, producing decreases in acute phase proteins (which contribute to the globulin fraction), and increases in negative acute phase protein (albumin). However, no adverse biological outcomes have been associated with such changes in these serum proteins according to the registrant. Therefore, these changes in serum proteins in high dose males and females were considered test article-related although they were not considered biologically relevant by the registrant based on their small magnitude and lack of association with known adverse outcomes. In addition to the serum protein changes noted above, minimal, statistically significant increases in albumin/globulin ratio were present in the 1 mg/kg/day males (+16%) and 50 mg/kg/day females (+9%) at all intervals. Also, in some individual animals in these groups, albumin tended to be higher and globulin lower than controls. However, group mean albumin and globulin in these groups were not statistically different from controls (with the exception of elevated albumin in the 1 mg/kg/day male group at 12 months and decreased globulin in the 50 mg/kg/day female group at 6 months), and differences from control group means for both albumin and globulin were $\leq 8\%$ at all intervals. Therefore, the statistically significant changes in albumin/globulin ratio in these groups were also considered by the registrant to be test article-related but non-adverse based on the minimal nature of the changes. However, the changes in albumin and albumin/globulin ratio are indicative of effects on the acute phase response of the immune system. These effects were also observed with other PPAR- α inducers, occurs in humans and is secondary to binding to the PPAR- α receptor (Gervois et al, 2004). Therefore, these effects are considered adverse by the RIVM.

Phosphorus was statistically higher than control in the 500 mg/kg/day female group at the 12-month interval. The relationship to treatment for this difference is uncertain; however values in individual rats in this group were similar to controls except for one animal, and there were no statistically significant changes in phosphorus in any treated group at any other time point. Therefore, based on the minimal nature of these changes, they were not considered to be adverse. Phosphorus was statistically higher in the 0.1 at the 3-month interval and 50 mg/kg male groups at the 3 and 6-months interval and non-significantly after 12-

months. These differences at 0.1 mg/kg bw/day were considered to be unrelated to test article administration since they did not occur in a dose-related manner and there were no statistically significant differences in phosphorus in any treated group relative to control at the 6- and 12- month intervals. Calcium was statistically higher in the 50 mg/kg/day males at the 12-month interval. One fraction of serum calcium exists as "bound" to albumin, and increases in albumin are necessarily associated with physiologically appropriate increases in calcium. Changes in bound calcium have no effect on unbound ("ionized") calcium, which is the physiologically active form of calcium. Therefore, the increase in calcium in the 50 mg/kg/day male group at 12 months was considered to be secondary to albumin changes, physiologically irrelevant, and thus non-adverse. Urea nitrogen was statistically higher than the respective control in the 50 mg/kg/day male group at the 3 and 6-month interval. These differences were not consistent across time, and there were no correlative changes in related clinical chemistry parameters or with microscopic changes in the kidneys. Chloride was statistically higher than control in females at 1 and 500 mg/kg/day (but not at 50 mg/kg/day) at the 6-month interval. These differences were not considered to be test article-related as they very slight (only 2% above control), did not occur in a dose-related manner, and were not associated with changes in chloride at any other interval.

In females receiving 500 mg/kg/day, minimal, statistically significant increases in urine volume and pH and decreases in urine specific gravity-suggestive of a minimal diuresis-were present at both the 6- and 12-month intervals. Although minimal and not associated with changes in kidney-related chemistry parameters (e.g., urea nitrogen, creatinine), these changes may be correlative to increased incidences and severity of chronic progressive nephropathy observed microscopically in this dose group at the 1-year interim sacrifice. Urine pH was increased and urine volume after 12-months decreased in males at all dose levels. These changes are of uncertain relationship to administration of the test article based on the lack of a clear dose response across the affected groups. Based on the lack of any correlative findings suggestive of an effect on the urogenital system, the changes were considered nonadverse. In addition, no such effects were observed in males in the 90-day study up to 100 mg/kg bw/day.

Interim: Test article-related organ weight changes were limited to the high dose groups. Increased liver weights occurred in males at 50 mg/kg/day and in female rats at 500 mg/kg/day. In males, the increase was small and only the mean liver relative to body weight was statistically significantly increased (14.53% above control). In females, the liver weight increase was larger (mean liver relative to body weight was 66.75% above control) and all parameters (absolute and relative to both brain and body weight) were statistically significantly increased. The liver weight changes in the affected male and female groups were associated with microscopic changes in the liver (discussed below). Mean final body weight at the interim necropsy was 19.51% less than control in the 500 mg/kg/day females. As a result of this decrement in mean final body weight, the brain, kidney, and thyroid/parathyroid relative to body weight were statistically significantly increased. Aside

from a slight increase in severity of chronic progressive nephropathy in the kidneys, there were no microscopic changes in these organs associated with the increased weights, and mean absolute weights were not increased. Thus, these changes were considered secondary to the body weight decrement at 500 mg/kg/day. Additionally, mean absolute and relative to brain weights of the spleen in the 500 mg/kg/day females were statistically significantly lower than controls. These differences were not considered test article-related by the registrant, as there were no microscopic changes in the spleen in either sex.

Terminal: No test article-related or statistically significant organ weight changes occurred in males. In females, the only test article-related effect on organ weights was an increase in liver and kidney weights at 500 mg/kg/day. Mean absolute and relative to both body and brain weights were increased compared to control, with mean liver relative to body weight 41.61% greater than control. There were several test article-related microscopic changes to account for the increased weights, as described below. Absolute and relative to bodyweight kidney weights were increased and related to microscopic changes.

Interim: A test article-related macroscopic observation, "irregular surface" of the kidneys, was noted in the kidneys of one 500 mg/kg/day (high dose) female. This observation correlated with mild chronic progressive nephropathy in this animal and was indicative of a slight increase in severity of chronic progressive nephropathy in the 500 mg/kg/day female group at one year.

Terminal: No test article-related macroscopic observations were noted in males. In females, test article-related macroscopic observations were noted in the kidneys and liver. In the kidneys, "irregular surface" was noted in 16 of 70 animals at 500 mg/kg/day (not present in controls or any of the lower dose groups), while in the liver, "tan focus/foci" was noted in 1, 1, 1, and 8 of 70 animals each at 0, 1, 50, and 500 mg/kg/day, respectively, and "mass/nodule" was noted in 14 of 70 animals at 500 mg/kg/day (not present in controls or any of the lower dose groups). These macroscopic observations were correlative to test article-related microscopic findings described below.

Interim: Test article-related microscopic findings were noted in the liver of both male and female rats, and in the kidneys of females, in the high-dose groups (50 and 500 mg/kg/day for males and females, respectively). In males, there was a slight increase in minimal focal cystic degeneration of the liver (0, 0, 0, and 3 at 0, 0.1, 1, and 50 mg/kg/day, respectively). This finding was more pronounced in the terminal portion of the study. Also in males, there was a slight increase in minimal to mild focal necrosis of the liver (1, 1, 0, and 5 at 0, 0.1, 1, and 50 mg/kg/day, respectively). In females, the only microscopic finding in the liver was centrilobular hypertrophy, which occurred in all 10 of the 500 mg/kg/day females. This change was of minimal or mild severity and was characterized primarily by a slight increase in size of centrilobular hepatocytes with increased red granularity to the cytoplasm and is consistent with peroxisome proliferation. Also in females, there was a very slight increase in incidence and severity of chronic progressive nephropathy in the kidneys at 500 mg/kg/day. This

change was characterized by foci of basophilic tubules, some with thickening of basement membranes. In the 500 mg/kg/day group, most incidences were of mild severity, while in the other groups, including controls, the incidences were primarily of minimal severity, although in a single control female the incidence was of moderate severity. In males, there was a single interstitial cell adenoma of the testes at 50 mg/kg/day; incidences of interstitial cell hyperplasia were 1, 0, 0, and 3 at 0, 0.1, 1, and 50 mg/kg/day. The incidences of these changes in treated groups were not statistically different from controls (historical data for rats of this age were not available). Proliferative interstitial cell lesions are discussed in more detail under microscopic findings for the terminal sacrifice. All other microscopic findings were considered incidental, and typical of those seen in rats of this strain and age.

Terminal: Test article-related non-neoplastic microscopic changes were observed in the liver and adrenal of males and in the liver, kidneys, nonglandular stomach (limiting ridge), and tongue of females at the highest doses tested, 50 mg/kg/day in males and 500 mg/kg/day in females. Focal vacuolation of the adrenal in males was reduced at all dose levels compared to controls but showed no dose response relation. Therefore, this effect was not considered substance related. In the liver of males at 50 mg/kg/day there were statistically significantly increased incidences of focal cystic degeneration, centrilobular hepatocellular hypertrophy, and centrilobular hepatocellular necrosis. Periportal liver vacuolation was reduced. Cystic degeneration was characterized by the presence of multilocular cystic spaces containing finely granular or flocculent material without endothelial or epithelial cells lining the spaces. Centrilobular hypertrophy, morphologically consistent with peroxisome proliferation, was characterized by hepatocytes with red granular cytoplasm sometimes containing small amounts of pigment morphologically compatible with lipofuscin. Centrilobular hepatocellular necrosis was typically of the coagulative type with strongly eosinophilic-staining cytoplasm and pyknotic nuclei. Test article-related findings in the liver of females at 500 mg/kg/day were similar to those noted in males at 50 mg/kg/day, and also included low incidences of panlobular hepatocellular hypertrophy and individual cell hepatocellular necrosis. Panlobular hepatocellular hypertrophy was characterized by enlargement of hepatocytes (as described above for centrilobular hypertrophy) throughout the entire liver. Individual cell necrosis was characterized by the presence of scattered single hepatocytes with features characteristic of apoptosis. Liver periportal vacuolation was reduced at the highest dose in females.

Statistically significantly increased microscopic findings in the kidneys of females at 500 mg/kg/day included tubular dilatation, oedema of the renal papilla, transitional cell hyperplasia in the renal pelvis, tubular mineralization, renal papillary necrosis, and chronic progressive nephropathy. Tubular dilatation frequently occurred in an ascending pattern extending from the papilla to the outer cortex, while at other times it was more prominent in the papilla. Oedema of the papilla was characterized by increased rarefaction or myxomatous change in the papillary interstitium, sometimes with polypoid protrusions from the lateral surface of the papilla. The oedema and tubular dilatation were often associated with hyperplasia of the transitional cell epithelium lining

the papilla and pelvis. In some animals, necrosis of the tip of the papilla was present. In some 500 mg/kg/day females with the renal papillary changes, lesions diagnosed as chronic progressive nephropathy (CPN) were comprised of dilated tubules (often in an ascending pattern as described above), mononuclear cell infiltrates, and basophilic tubules, but with less thickening of tubular basement membranes than typically seen in CPN. In these animals, the constellation of lesions diagnosed as CPN may be more representative of retrograde nephropathy, rather than typical CPN.

The nonglandular stomach (limiting ridge only) and the tongue had statistically significantly increased incidences of hyperplasia of squamous epithelium at 500 mg/kg/day. In the tongue, subacute/chronic inflammation occurred in association with squamous epithelial cell hyperplasia. There is no data describing incidence of epithelial hyperplasia of the limiting ridge of the nonglandular stomach in the historical control database for 2 year studies. The incidence of squamous cell hyperplasia of the tongue at 500 mg/kg/day (18.6%) exceeds the historical control range of 0-3.3%. There was also a single incidence of squamous cell carcinoma (1.4%) in the tongue of females at 500 mg/kg/day. This is well within the historical control range of 0-1.7% and the finding of a single such tumour was not considered a direct result of test article administration.

A statistically significant increase in the incidence of alveolar histiocytosis was present in females at 500 mg/kg/day. The incidences were 22, 20, 21, 42 (61%) at 0, 1, 50, and 500 mg/kg/day, respectively. The incidence at 500 mg/kg/day was statistically significant by both the Fisher Exact test and the Cochran-Armitage trend test and is at the upper end of the historical control range of 9.2-61.7%. The increased incidence of this common background finding may be secondary to aspiration of dosing formulation at this high concentration; however, a definitive mechanism for this increase could not be determined. A slight but statistically higher (by the Cochran-Armitage Trend test) incidence of pancreatic acinar cell hyperplasia occurred in females at 50 and 500 mg/kg/day; incidences were 0, 2, 5, 5 (7.1%) at 0, 1, 50, and 500 mg/kg/day, respectively. The incidences of acinar cell hyperplasia at the two highest doses slightly exceeded the historical control range of 0-4.6%, but were not significant by the Fisher Exact test and were not associated with pancreatic acinar cell tumours. In addition, acinar cell hyperplasia did not occur in a clear dose response manner, as incidences in the 50 and 500 mg/kg/day groups were the same despite the order of magnitude difference in dose. In contrast, all other test article-related changes observed at 500 mg/kg/day occurred with a clear dose response. Therefore, the slight increase in acinar cell hyperplasia in the 50 and 500 mg/kg/day females was considered by the registrant most likely spurious and not test article-related. A statistically significant increase (by both the Fisher Exact test and the Cochran-Armitage trend test) in the incidence of alopecia/hypotrichosis was present in females at 500 mg/kg/day. The incidences were 1/70, 2/48, 5/55, and 9/70 (12.9%). However, the relevance of alopecia/hypotrichosis is more appropriately made by interpretation of the incidence of this finding in the clinical observations of the study

rather than the microscopic observations. Therefore, for microscopic purposes, this was not considered at potential target organ.

Finally, incidences of cataract of the lens of the eye, pelvic mineralization of the kidney, and angiectasis of the liver were statistically significantly increased. Cataract of the eye and angiectasis of the liver were statistically significantly increased by the Cochran-Armitage trend test at 500 mg/kg/day while pelvic mineralization of the kidney was statistically significantly increased by the Cochran-Armitage trend test and Fisher's exact test at 500 mg/kg/day, and Fisher's exact test at 1 mg/kg/day. Incidences of cataract of the eye were 0/69, 0/48, 0/55, and 3/70 (4.29%) at 0, 1, 50, and 500 mg/kg/day, respectively. The historical control range for cataract is 0 to 10.8%. Incidences of pelvic mineralization of the kidney were 52/70, 63/70, 58/70, and 63/70 (90.0%) at 0, 1, 50, and 500 mg/kg/day, respectively. The historical control range is 45.0 to 87.7% (note: two studies in the historical control database with an incidence of 0/60 reflect that this change was simply not tracked as pelvic mineralization in the studies). Incidences of angiectasis of the liver were 1/70, 0/70, 3/70, and 5/70 (7.14%) at 0, 1, 50, and 500 mg/kg/day, respectively. The historical control range is 0 to 10.0%. For each of the changes, the incidence was well within the historical control range, except pelvic mineralization, which is a very common background finding, only slightly exceeded the historical control range. Thus, these changes were not considered test article-related.

This study was used as a key study in the REACH registration dossier for repeated dose toxicity and carcinogenicity. A NOAEL of 1 mg/kg bw/day for male rats was established by the registrant based on liver effects and equivocal increases in pancreatic and Leydig cell tumours. For female rats, a NOAEL of 50 mg/kg bw/day was established by the registrant, based on reductions in body weight and body weight gain, mild decrease in red cell mass, effects on the liver, kidneys, nonglandular stomach and tongue, and increase in liver tumours. The RIVM derives a NOAEL of 0.1 mg/kg bw/day based on an increase in A/G ratio in males at the next higher dose level of 1 mg/kg bw/day.

A1.9 Mode of action

In view of the RIVM, the observed effects with FRD-902 including increased beta-oxidation, liver hypertrophy, reduction in serum cholesterol, increased albumin / globulin ratio and observed tumour types are typical for peroxisome proliferators. Peroxisome proliferators act mainly by binding to the peroxisome proliferator-activated receptor alpha (PPAR- α). However, no direct information on the interaction of FRD-902 with PPAR- α is available. A large volume of information on this interaction is available for the structural analogue PFOA which induces comparable effects in repeated dose toxicity studies and carcinogenicity studies. The results indicate that substances like PFOA and therefore possible also FRD-902 can interact also with other nuclear receptors. According to published reviews, the human relevance of the hepatic and carcinogenic effects of PFOA cannot be excluded (EFSA, 2008) (US-EPA, 2016) (IARC, 2011) (IARC, 2016). Therefore, the observed effects with FRD-902 are also considered relevant for humans.

Annex 2. Human health toxicity E1

Kinetics

Three male rats (CrL:CD(SD), 6-8 weeks old) were orally exposed (gavage in water) once to 20 mg E1/kg bw. The concentration of E1 in urine collected at several time points after exposure was determined using GC/MS. The E1 concentration in urine was below the LOD of 0.04 ug/mL or below the LOQ of 0.02 ug/mL in all animals at all time points (Anonymous, 2007). This is a very limited report. It is unclear how the rats were dosed as the stated concentration of 5 mg E1/ml water is above the water solubility of 7 mg/L.

Three male and three female rats (CrL:CD(SD), 7-12 weeks old) were orally exposed (gavage in water) once to 10 or 30 mg E1/kg bw. E1 was determined in blood samples at 14 time points after administration and once before administration and in liver and fat samples after necropsy. E1 plasma levels were below the LOQ (LOQ level not stated) at all time points. Also all liver samples were below the unstated LOQ. Some fat samples appeared to contain low concentration of E1. The results (not stated) were not proportional with dose or consistent within or across the sexes. The spectrum of the analyte could not be confirmed (Anonymous, 2008). This is a very limited report lacking details on the LOQs and the measured concentrations.

In an in vitro test on metabolism using male rat S9 no metabolism and difference between active and heat treated S9 was observed indicating absence of metabolism. This study was not provided but is available upon request.

Acute Toxicity

In an acute oral toxicity study a single male rat was exposed to 7500, 11000, 17000 or 25000 mg/kg bw E1 by gavage. The rats were observed for 14 days after which liver weight was determined and liver histopathology performed. No mortality occurred but some limited toxic signs were observed. No effects upon final body weight, liver weight or liver pathology was observed (Anonymous, 1967a). This is a very limited report of a study using only a single animal per dose whereas normally several rats per dose levels are required to estimate the LD₅₀.

Rabbits dose dermally with 25000 or 37500 mg/kg bw E1 did not display mortality or systemic histopathological effects. Slight CNS effects occurred during exposure. Local irritation in the form of reversible erythema was observed. This study was not provided but is available upon request.

In an acute inhalation toxicity study groups of 4 male rats (Chr-CD) were exposed whole body for 4 hours to E1 at nominal concentrations of 5000, 15000 or 30000 ppm as a vapour. The rats were observed for 14 days after which the relative liver weight and lung pathology was determined. No mortality was observed. Clinical signs of toxicity exhibited during exposure were mild lacrimation, red ears, inactivity and deep respiration at the highest concentration with lesser effects at lower

concentrations. There was no effect on relative liver weight. Mild irregular lung congestion was observed at the two highest concentrations at 14 days after the exposure (Anonymous, 1965). The study report was very limited.

In an acute inhalation toxicity study groups of 6 male rats (Chr-CD) were exposed whole body for 4 hours to E1 at nominal concentrations of 5870, 13130 or 23540, 62226 or 195114 ppm as a vapour. Some of the tested batches of E1 contained a mixture of n-propyl and isopropyl isomers. At E1 concentrations above 100000 ppm, additional oxygen was supplied to enrich the air. The post exposure period was not stated. No mortality occurred. Several clinical effects were observed during exposure including tremor and convulsions but not after exposure. The clinical effects indicate respiratory irritation and possible effects on the central nervous system (Anonymous, 1967b).

In an acute inhalation toxicity study groups of 6 male rats (Chr-CD) were exposed whole body for 4 hours to E1 at nominal concentrations of 396800 or 576000 ppm as a vapour. Additional oxygen was supplied to enrich the air up to 20% oxygen. Gross and histopathological examination was performed on day 1,2 and 7 of exposure on 2 rats per dose. No mortality occurred. Several clinical effects were observed during exposure including tremor but not after exposure. The clinical effects indicate respiratory irritation and possible effects on the central nervous system. No histopathological changes were observed in a range of tissues including liver and lungs (Anonymous, 1968).

An additional acute inhalation study in dogs challenged with epinephrine resulted in a NOAEC of 100000 ppm and a LOAEC of 200000 ppm. This study was not provided but is available upon request.

Repeated dose toxicity

In a two-week repeated dose inhalation study, groups of 10 male rats (CrL:CD@BR) were exposed whole body during 10 days for 6 hours a day to nominal concentrations of 0, 5000, 25000 or 175000 ppm E1 as a vapour. Additional oxygen was supplied at the highest dose level to ensure an oxygen content of at least 19%. The test atmosphere was produced by evaporation of E1 and resulted in mean analytical concentrations within 1% of the target concentration. Necropsy was performed on 5 rats per group directly after the last exposure whereas the other 5 rats were sacrificed 2 weeks after the last exposure. The determined parameters included body weights, clinical effects, hematology, clinical chemistry, urine analyses and macroscopic and microscopic pathology. In addition, micronuclei were determined as described below.

The mean analytical concentration was within 1% of the nominal concentration. No mortality or effects on body weight were observed. There were no changes in hematology, clinical chemistry, organ weights and urine analyses. A compound-related increase in the hyaline droplets within kidney tubules of 3 out of 5 rats exposed to 175000 ppm was observed microscopically. This observation in the kidney was minimal in severity, unaccompanied by cell necrosis, and judged not to be biologically or toxicologically significant by the authors. A lack of response to an alerting stimulus and occasional tremors was observed

during exposure at the highest concentration. The NOAEC is determined at 25000 ppm. The absence of an increase in fluorine in urine compared to controls indicates the absence of metabolism resulting in the release of fluorine from E1 (Anonymous, 1995).

Mutagenicity

In an in vitro study on the mutagenicity of E1 in *Salmonella typhimurium* (Ames test, OECD 471) using strains TA100, TA1535, TA97 and TA98 with and without exogenous metabolic activation, no increase in reverse mutations was observed at dose levels up to 5000 ug/plate (Anonymous, 1994). However, considering the low water solubility of the substance and the high vapour pressure of the substance it is deemed likely that most E1 evaporated from the plates during incubation at 37°C, as taping of the plates to reduce evaporation is not mentioned. Therefore, this study cannot be used to demonstrate the absence of a mutagenic potential.

In an additional bacterial reverse mutation test of E1 in *Salmonella typhimurium* (Ames test, OECD 471) using strains TA100, TA1535, TA97 and TA98 and *Escherichia coli* using strain WP2 uvrA⁻ with and without exogenous metabolic activation, no increase in reverse mutations was observed at dose levels up to 5000 ug/plate (Anonymous, 2009). Pre-incubation was performed using ice cold E1 in acetone in sealed test tubes and plates were sealed with a vinyl sack per concentration and experimental condition to minimise evaporation. The study was negative.

In an in vitro test for chromosome aberrations in human lymphocytes, E1 was stated to be negative with and without metabolic activation. However, considering the low water solubility and the high vapour pressure it is deemed likely that E1 evaporated from the culture vessel during incubation. Therefore, this study cannot be used to demonstrate the absence of a mutagenic potential. This study was not provided but is available upon request.

An in vivo micronucleus test was performed as part of a two week inhalation study as described above. An additional group containing 5 male rats exposed by IP injection to cyclophosphamide 24 hours before necropsy was included as positive control. Directly after the last exposure, bone marrow smears were prepared. Two thousand PCEs per animal were evaluated for micronuclei after staining with acridine orange. In addition, the PCE/NCE ratio was determined. No increase in micronuclei or change in the PCE/NCE ratio was observed except for the positive control (Anonymous, 1995).

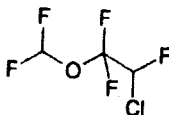
Read-across

Read-across from FRD-902 to E1 is not justified because of the differences in chemical-physical properties (solid versus liquid with high vapour pressure, acid or salt versus neutral, more lipophilic substance). In addition, the available toxicological data indicate that E1 is less toxic than FRD-902. For example the acute oral LD50 of FRD-902 was 1750 mg/kg bw in male rats. This is at least 10-times below the LD50 of E1 in male rats.

Several expert systems including 'Oncologic', 'OECD toolbox' and 'ISS' indicate that E1 is an alpha, beta-haloether or alpha haloether which could be direct-acting alkylating agents leading to mutagenicity and carcinogenicity. However, the alert is based on chloro-ethers, limited to monohalo methyl or ethyl ethers and probably less relevant for fluoro-ethers as the C-F bond is more stable and less relevant for di halo ethyl or methyl ethers. In addition, no in vivo mutagenicity was observed for the FRD-902, which also fulfils the alpha haloether alert, and the carcinogenicity was limited to an increased number of tumours typical for peroxisome proliferators in rats. This confirms the limited relevance of the alert for fluoro-ethers. Overall, the expert systems do not indicate a strong concern for mutagenicity or carcinogenicity. However, these systems are only designed to detect (sub) structures that could result in a specified effect but not for identifying the absence of effects. Therefore, mutagenic and carcinogenic properties cannot be excluded based on read-across.

Read-across based on structural analogues as identified using the OECD QSAR toolbox indicates limited toxicity after repeated dose inhalation exposure. Two fluorinated ethers were identified as the closest analogues and are shown below. However, both contain one chlorine atom instead of only fluorine atoms. As the bond between fluorine and carbon is stronger than between chlorine and carbon, the reactivity and toxicity is expected to be lower for the fluorinated compound. Therefore, these analogues have some benefit for the assessment of E1.

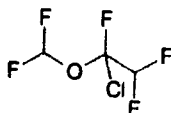
1. Enflurane



CAS: 13838-16-9 EINECS: 237-553-4

Name: Enflurane; ethane, 2-chloro-1-(difluoromethoxy)-1,1,2-trifluoro-. Enflurane is an inhalation anaesthetic used for narcosis in concentrations of 5000 to 15000 ppm. A MAK value of 20 ppm (150 mg/m³) is available (<http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb1383816e0009/full>). The kinetic data show limited metabolism.

2. Isoflurane

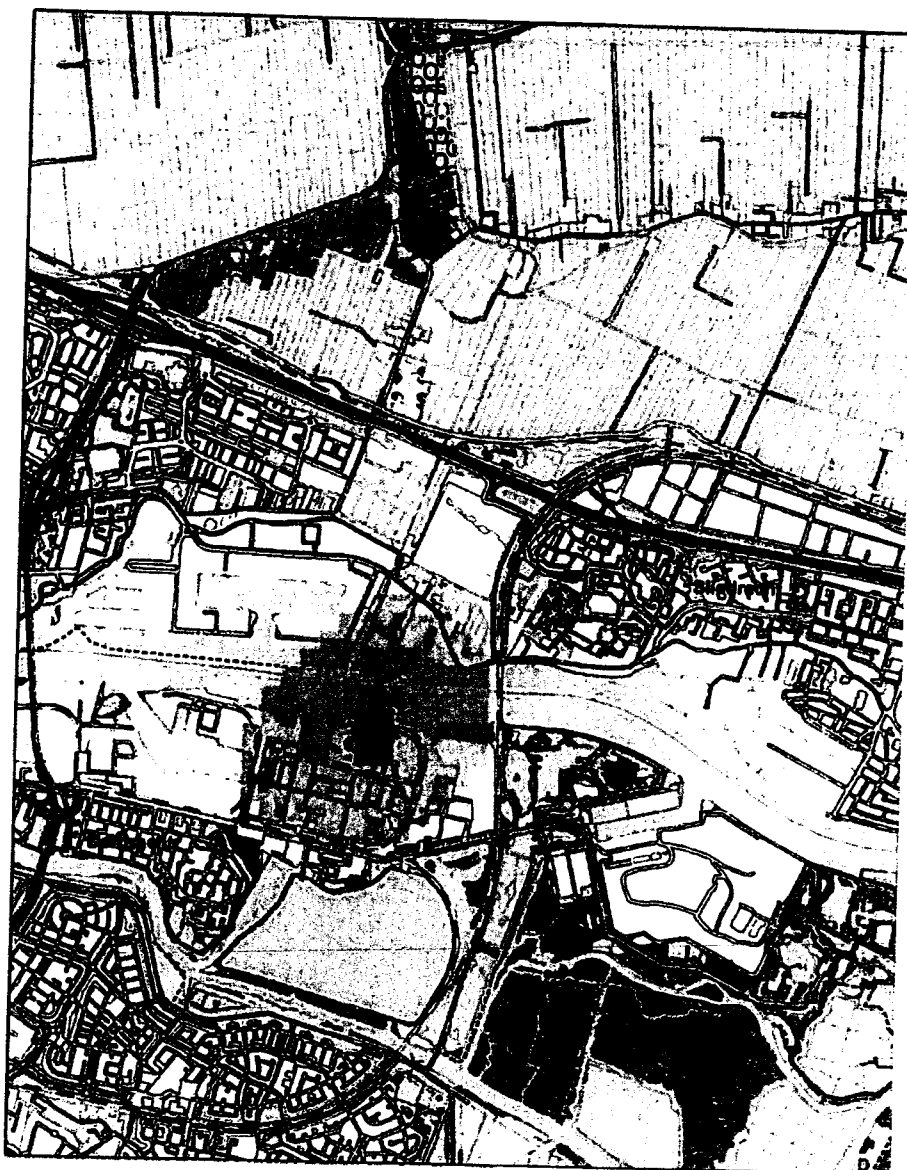


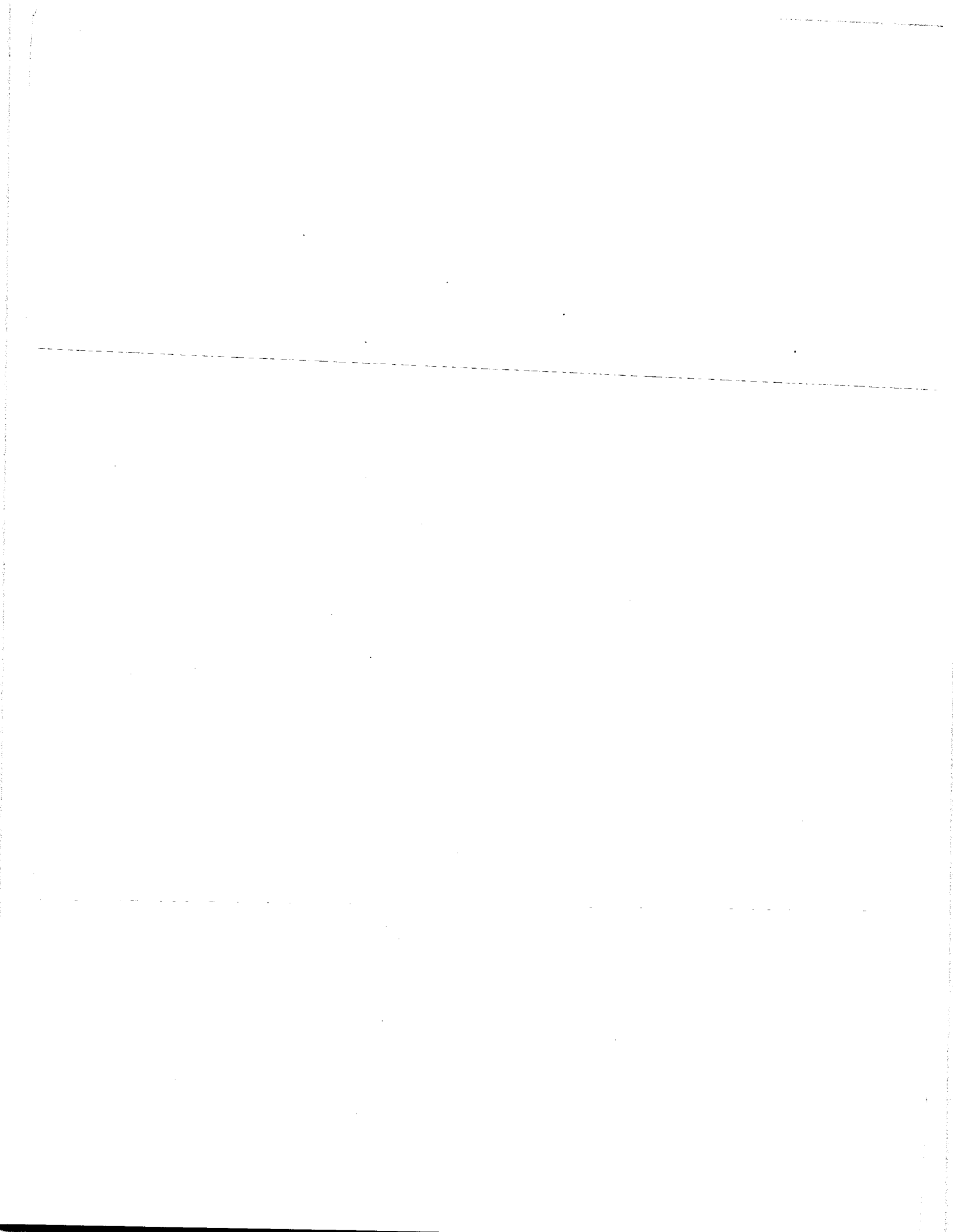
CAS: 26675-46-7 EINECS: 247-897-7

Name: Isoflurane; 2-chloro-2-(difluoromethoxy)-1,1,1-trifluoroethane. Isoflurane is an inhalation anaesthetic used for narcosis in concentrations of 12000 or 23000 ppm. No MAK was derived because the available database was inadequate (<http://onlinelibrary.wiley.com/doi/10.1002/3527600418.mb2667546e0007/full>). The NOEL from chronic studies in mice was 1000 ppm (7470 mg/m³) and nervous system effects were observed in humans after brief exposures to 1150 ppm.

In addition, information on fluorinated compounds was collected from the RepDose database (Frauenhofer). However, the available fluorinated alkanes did not contain ethers and no general conclusion on the repeated dose toxicity via inhalation could be determined as the NOEC values from these studies varied more than 1000 fold but all NOECs were above 50 ppm. Overall, the information on analogues indicates limited toxicity for E1.

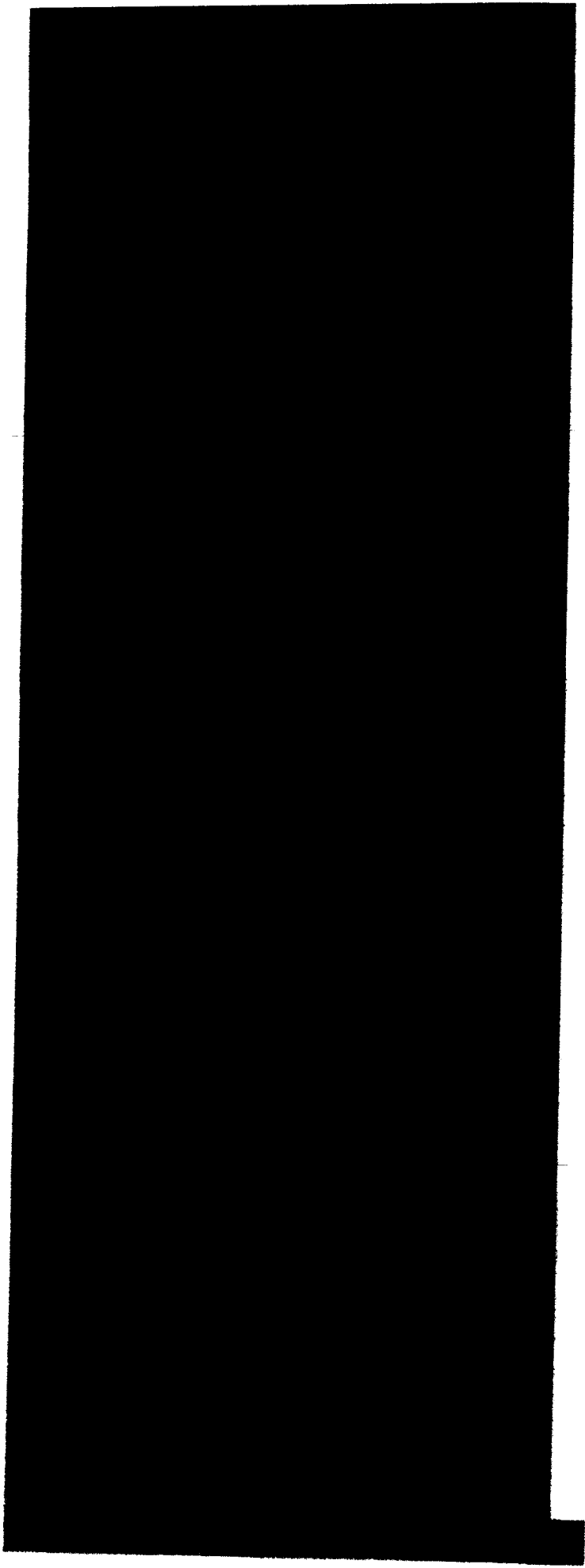
Annex 3. Calculated air concentrations FRD-903 based on the permitted emissions (in ng/m^3)





RIVM

Committed to health and sustainability



DRAFT

- Historically (1950 – Present) have participated in drinking water research into the effectiveness of new chemicals in purifying drinking water for potable use. The present era of identifying potential contaminants of emerging concern aims at determining plant removal efficiencies of these compounds so as to plan for future regulatory excellence (CIP, Treatment Upgrades, etc..)
- CFPUA working with Dr. Detlef Knappe on identifying high levels of in Bromide in the Cape Fear River. Concern because elevated Bromide is linked to elevated (Brominated) THM's and potential for Bromate production via our Ozone Process. We are regulated as an Ozone Plant on Finished Bromate.
- GOALIE project signed August 2015 – Mike Richardson was lead CFPUA Contact for Project.
- Helped us to understand DBP formation potential, and Bromate formation potential.
- Along with bromide samples, 1/2 samples went to EPA lab to be tested for PFAS.
 - Data obtained from this sampling was basis for paper that was written and published.
- May 3, 2016 – CFPUA contact Mike Richardson received Draft of PFAS paper. This draft paper which was ultimately published November 10, 2016 in Environmental Science and Technology Letters is a component of a broader NSF study being conducted by Dr. Knappe that remains underway.
- August 11, 2016 – Contacted by Mike Richardson regarding a statement being crafted by Mike McGill concerning PFAS. *→ what prompted Mike R. to tell Mike M.*
 - Statement to be used if asked about the study or feel it is necessary to get out in front of the story.
 - Ben Kearns provided available PFAS data (UCMR3) to support language in the statement.
- September 18, 2016 – Pre-Submission Final-Draft PFAS Study to contributing utilities for co-authorship.
- September 25, 2016 – Responded to Dr. Knappe with Mike Richardson authorizing us as co-authors.
- September 30, 2016 – Mike Richardson (Water Resource Manager) retired.
- September 28th – October 8th, 2017 - Hurricane Matthew emerges and directly impacts area.
- October 13th – Mid November 2017 – Lower Cape Fear Raw Water Line Rupture and response.
- October 24th, 2016 – Ben Kearns requests EMD to conduct annual monitoring (Special Sweeney Post Sampling) for EPA Method 537 at Monthly Sampling Meeting. *group of fluorinated compounds, not BenX*
- November 8, 2016 – EMD sampled Sweeney entry point to distribution (EUROFINS - EPA method 537) – due to the potential for future regulatory action on these chemicals and to obtain site specific background data.
- November 10, 2016 – Dr. Knappe PFAS Study published in Environmental Science and Technology Letters Journal.
 - Authors included Mark Stynar and Andrew Lindstrom with EPA and contributing utilities.
- March 2, 2017 – Dr. Knappe contacted Ben Kearns to discuss the published results of PFAS paper as well as current and future implications/sampling/research into the topic. Inquiring as to who

should be the point of contact for CFPUA in absence of Water Resource Manager. (Ben K. Requested published version of paper at this time.)

- March 3, 2017 – Ben Kearns obtained copy of published paper from Dr. Knappe for in-depth review and analysis following his direct conversations March 2nd.
- March 7, 2017 - Obtained additional peer reviewed research on PFAs compounds from Dr. Knappe and began sourcing other studies related to compounds identified in study.
 - Also, requested that EMD look into contract labs who can analyze the compounds identified in the PFAs study (Specifically New PFASs identified)
- March 23, 2017 – contacted Dr. Knappe and coordinated his attendance at our April 19th Water Team Meeting at Sweeney WTP to discuss his research, the findings of the published paper, and desired future sampling with CFPUA.
- April 13, 2017 – Conducted meeting with middle/upper management regarding study, findings, and any appetite for additional sampling participation.
 - Presentation Notice sent to Water Team Distribution E-mail List regarding April 19th
- (Date Unknown) Frank Styers contacted Dr. Knappe to discuss study implications.
- April 19, 2017 – Dr. Knappe Presentation at Water Team Meeting held at Sweeney WTP. Ben Kearns led meeting as John Malone was out of town.
 - Dr. Knappe Presentation disseminated to Water Team E-mail List for those not in attendance same day.
 - Note* - A PWS Representative was in the meeting as they have a standing invitation to all Water Team Meetings.
- April 22, 2017 – Obtained recent peer reviewed study from Dr. Knappe regarding GenX toxicity out of Stockholm University in Sweden.
- April 25, 2017 – Notified by Dr. Knappe that a reporter from the Star News (Vaughn Hagerty) was requesting information on the compounds which turned up in his published paper.
- April 27, 2017 – Beth obtained copy of Chemora NPDES Permit from Jim Gregson with DEQ.
- May 1, 2017 – Frank Styers requested update from Ben Kearns on status of proposal from Dr. Knappe regarding proposed additional sampling at Sweeney.
 - Frank was notified that we are still awaiting detailed sampling plans from Detlef for review.
- May 16, 2017 – Notified again by Detlef that the reporter was still inquiring and passed on this information to Beth and John Malone regarding the inquiry.
- June 2, 2017 – Board update statement discussion/working meeting regarding PFASs from Frank via email.
 - Held at Sweeney WTP Training Room where supplementary information on PFASs was provided.

→ Ben sent to Beth

Ben, Frank, John Malone & Ben K. question re: methods, data validity

Hindi

April 19th - Mike McGill's last day.

John Malone

From: Frank Styers
Sent: Friday, June 16, 2017 2:50 PM
To: John Malone; b@cfpua5.onmicrosoft.com
Subject: Fwd: PFASs in the Cape Fear River watershed
Attachments: PFECAs_Sun_ESTL2016.pdf; ATT00001.htm; PFECAs_Sun_ESTL2016_SI.pdf; ATT00002.htm

Sent from my iPhone

Begin forwarded message:

From: "Detlef Knappe" <knappe@ncsu.edu>
To: "Frank Styers" <Frank.Styers@cfpua.org>
Subject: Fwd: PFASs in the Cape Fear River watershed

Frank,

I also sent this email.

Detlef

----- Forwarded Message -----

Subject: PFASs in the Cape Fear River watershed

Date: Wed, 23 Nov 2016 11:46:03 -0500

From: Detlef Knappe <knappe@ncsu.edu>

To: Hill, Tammy <tammy.l.hill@ncdenr.gov>, Adam Pickett <apickett@pittsboronc.gov>, aobriant@harnett.org <aobriant@harnett.org>, Austin, Vardry E <vardry.austin@ncdenr.gov>, Brower, Connie <connie.brower@ncdenr.gov>, Godreau, Jessica <jessica.godreau@ncdenr.gov>, Gore, Deborah <deborah.gore@ncdenr.gov>, Grzyb, Julie <julie.grzyb@ncdenr.gov>, Ham, Chad <chad.ham@faypwc.com>, Manning, Jeff <jeff.manning@ncdenr.gov>, Johnson, Chris <chris.johnson@ncdenr.gov>, Martie Groome <martie.groome@greensboro-nc.gov>, Michele Dawes <MDAWES@ci.asheboro.nc.us>, Poupart, Jeff <jeff.poupart@ncdenr.gov>, Risgaard, Jon <jon.risgaard@ncdenr.gov>, Sadosky, Rebecca <rebecca.sadosky@ncdenr.gov>, UCFRBA Kevin Eason <keason@ci.reidsville.nc.us>, UCFRBA Michael Rhone <mrhoney@ci.asheboro.nc.us>, Mick Noland <mick.noland@faypwc.com>

CC: Karoly, Cyndi <cyndi.karoly@ncdenr.gov>, Zimmerman, Jay <jay.zimmerman@ncdenr.gov>, Knight, Sherri <sherri.knight@ncdenr.gov>, Smith, Danny <danny.smith@ncdenr.gov>, Gregson, Jim <jim.gregson@ncdenr.gov>, Henson, Belinda <belinda.henson@ncdenr.gov>, Kroeger, Steve <steve.kroeger@ncdenr.gov>, tom.reeder@ncdenr.gov

Hello everyone,

I am attaching a paper we published this month in ES&T Letters. We studied the occurrence of per- and polyfluoroalkyl substances (PFASs) in the Cape Fear River watershed. Legacy PFASs, such as PFOA and PFOS dominated the PFAS signature in the Haw River. In contrast, new

fluorinated alternatives such as GenX, a replacement for PFOA, were very high in Wilmington (and by association also in Brunswick and Pender). None of the newly discovered compounds being discharged by the Chemours plant south of Fayetteville are removed by the advanced and conventional treatment processes employed in the Sweeney WTP in Wilmington. Also, many of the compounds are essentially non-adsorbable on activated carbon. I think it would be useful to discuss the results. A large number of people are exposed to high levels of PFASs through their drinking water!

Best regards,

Detlef

On 9/23/16 9:50 AM, Hill, Tammy wrote:

Hello!

I think you all know that Carrie Ruhlman has moved on from DWR. I'll be taking over coordination of the 1,4-dioxane monitoring project. Please feel free to contact me if I can be of assistance in this regard.

Attached are the results from DWR's quarterly surface water monitoring from January-July 2016. We will sample again in October, then prepare a summary report for October 2014-October 2016 data by the end of the year.

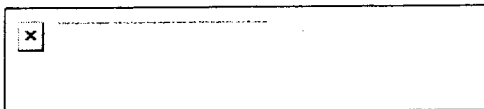
Warm regards,

Tammy Hill

Water Quality Data Analyst
NC Division of Water Resources – Water Sciences Section
NC Department of Environmental Quality

919 743 8412 office
919 743 8517 fax
Tammy.L.Hill@ncdenr.gov

1623 Mail Service Center
Raleigh, NC 27699-1623



Email correspondence to and from this address is subject to the North Carolina Public Records Law and may be disclosed to third parties.

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Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,^{*,†,‡,§} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||} Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

[†]Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

[‡]Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[§]National Exposure Research Laboratory, U.S. Environmental Protection Agency Research, Triangle Park, North Carolina 27711, United States

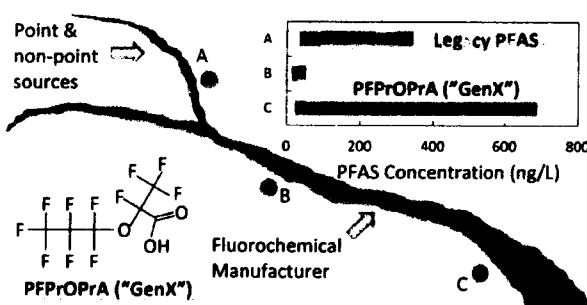
^{||}Cape Fear Public Utility Authority, Wilmington, North Carolina 28403, United States

[⊥]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n = 37$). Six other PFECAs were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain perfluoroalkyl sulfonic acids [$\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$; $n \geq 6$ (PFASs)] and perfluoroalkyl carboxylic acids [$\text{C}_n\text{F}_{2n+1}\text{COOH}$; $n \geq 7$ (PFCAs)] were predominantly used.² Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs^{3,4} has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health

advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.^{5,6} Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.^{7–10} Some fluorinated alternatives were recently identified,^{8,11} but others remain unknown^{12–14} because they are either proprietary or manufacturing byproducts.

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One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.¹¹ Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro-(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxa-octanoic) acid (PFO3OA), and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA alternative¹⁵ that has been produced since 2010 with the trade name "GenX". To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,¹⁵ and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),^{16–20} little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C–F bond makes PFASs refractory to abiotic and biotic degradation,²¹ and most water treatment processes are ineffective for legacy PFAS removal.^{22–27} Processes capable of removing PFCAs and PFASs include nanofiltration,²⁸ reverse osmosis,²⁵ ion exchange,^{28,29} and activated carbon adsorption,^{28,29} with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on powdered activated carbon (PAC).

MATERIALS AND METHODS

Water Samples. Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train [raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 20 L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4 °C until use in PAC adsorption experiments (background water matrix characteristics listed in Table S3).

Adsorption Experiments. Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 10–800%

of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 ppm) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 μ m, BET surface area of 1460 m²/g)³⁰ proven to be effective for PFAS removal in a prior study²⁹ was used at doses of 30, 60, and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

PFAS Analysis. Information about analytical standards and liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods for PFAS quantification is provided in the Supporting Information.

RESULTS AND DISCUSSION

Occurrence of PFASs in Drinking Water Sources. Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1.

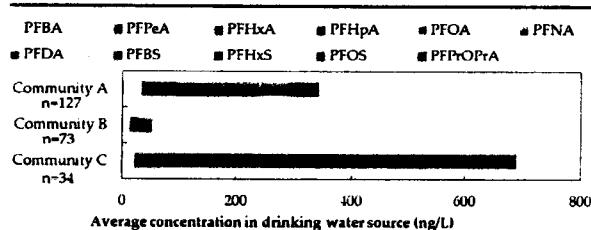


Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean Σ PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,³¹ suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80–85% C₆F_{2n+1}COOH; *n* = 7–9) in 2006 to short-chain (76% C₆F_{2n+1}COOH; *n* = 5–6) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.

Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLS, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QLS. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.³² However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

Fate of PFASs in Conventional and Advanced Water Treatment Processes. To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.^{22–26} The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.²⁵ Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400–500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2–113 times greater than that of PFPrOPrA (Figure 2b).

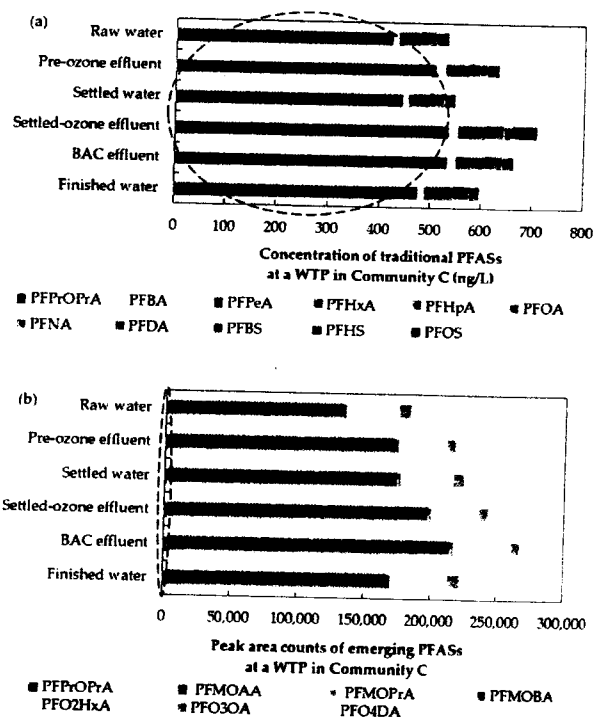


Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QLS were not plotted.

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

Adsorption of PFASs by PAC. PAC can effectively remove long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length.^{24,25,29} It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥ 7 . At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous

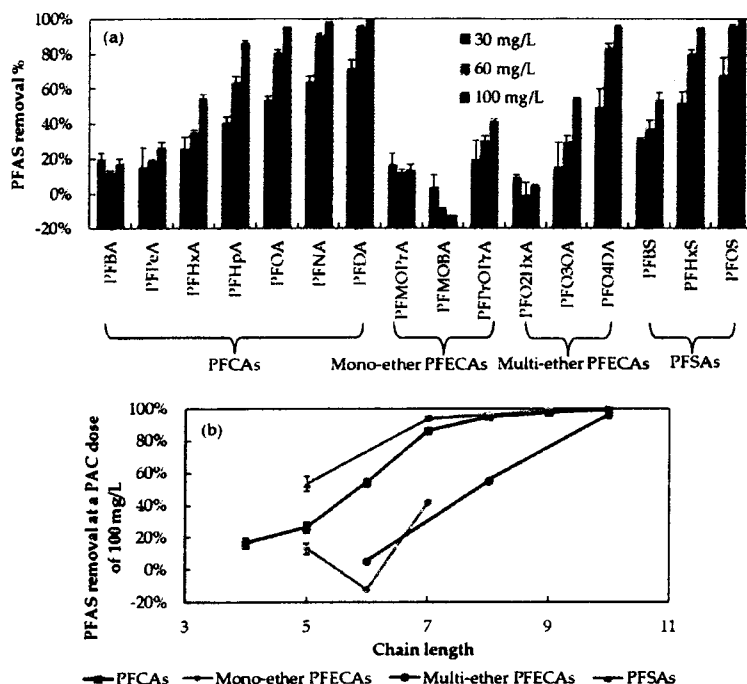


Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ~ 1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

studies.^{24,25,29} PFECAs exhibited adsorbabilities lower than those of PFCAs of the same chain length (e.g., PFMOBA < PFHxA), suggesting that the replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional CF_2 groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA \sim PFO2HxA, PFPrOPrA \sim PFO3OA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMOBA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFECAs removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: msun8@unc.edu. Phone: 704-687-1723.

ORCID[®]

Mei Sun: 0000-0001-5854-9862

Notes

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

The authors declare no competing financial interest.

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Supporting information

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Supporting information includes analytical method description, 6 tables, and 5 figures.

Mei Sun^{1,2}, Elisa Arevalo², Mark Strynar³, Andrew Lindstrom³, Michael Richardson⁴, Ben
Kearns⁴, Adam Pickett⁵, Chris Smith⁶, and Detlef R.U. Knappe²

¹Department of Civil and Environmental Engineering
University of North Carolina at Charlotte
Charlotte, North Carolina 28223, USA

²Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Raleigh, North Carolina 27695, USA

³National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711, USA

⁴Cape Fear Public Utility Authority
Wilmington, North Carolina 28403, USA

Analytical standards: PFASs studied in this research are listed in Table S1. For legacy PFASs, native and isotopically labeled standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA). No analytical standards were available for other PFECAs.

PFAS quantification: PFAS concentrations in samples from DWTPs and adsorption tests were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using a large-volume (0.9 mL) direct injection method. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC-MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5 μ m 100Å, Phenomenex Inc.) was used for PFAS analysis. The eluent gradient is shown in Table S4 in SI. All samples, calibration standards, and quality control samples were spiked with isotopically labeled internal standards, filtered through 0.45- μ m glass microfibre syringe filters, and analyzed in duplicate. The MS transitions for PFAS analytes and internal standards are shown in Table S5 in SI. The quantitation limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid, and 10 ng/L for other legacy PFASs and PFPrOPrA. The QL was defined as the first point of the standard curve, for which the regression equation yielded a calculated value within $\pm 30\%$ error. For PFECAs without analytical standards, chromatographic peak areas are reported.

PFAS concentrations along the treatment train of DWTP C were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Method details are described elsewhere.¹ The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAs without standards.

yl substances (PFASs) detected in the Cape Fear River (CFR) watershed

Compound	Molecular weight	Formula	CAS #	# of perfluorinated carbons	Chain length (including all C, O and S)
Perfluorocarboxylic acids (PFCAs)					
butanoic acid (PFBA)	214.0	C ₄ HF ₇ O ₂	375-22-4	3	4
pentanoic acid (PFPeA)	264.0	C ₅ HF ₉ O ₂	2706-90-3	4	5
hexanoic acid (PFHxA)	314.1	C ₆ HF ₁₁ O ₂	307-24-4	5	6
heptanoic acid (PFHpA)	364.1	C ₇ HF ₁₃ O ₂	375-85-9	6	7
octanoic acid (PFOA)	414.1	C ₈ HF ₁₅ O ₂	335-67-1	7	8
nonanoic acid (PFNA)	464.1	C ₉ HF ₁₇ O ₂	375-95-1	8	9
decanoic acid (PFDA)	514.1	C ₁₀ HF ₁₉ O ₂	335-76-2	9	10
Perfluorosulfonic acids (PFSAs)					
perfluorobutane sulfonic acid (PFBS)	300.1	C ₄ HF ₉ SO ₃	375-73-5	4	5
perfluorohexane sulfonic acid (PFHxS)	400.1	C ₆ HF ₁₃ SO ₃	355-46-4	6	7
perfluorooctane sulfonic acid (PFOS)	500.1	C ₈ HF ₁₇ SO ₃	1763-23-1	8	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)					
perfluoropropoxyacetic acid (PFMOAA)	180.0	C ₃ HF ₅ O ₃	674-13-5	2	4
perfluorobutyloxypropanoic acid (PFMOPrA)	230.0	C ₄ HF ₇ O ₃	377-73-1	3	5
perfluoropentyloxybutanoic acid (PFMOBA)	280.0	C ₅ HF ₉ O ₃	863090-89-5	4	6
perfluorohexyloxypropanoic acid (PFPrOPrA)	330.1	C ₆ HF ₁₁ O ₃	13252-13-6	5	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)					
perfluorooctanedioic acid (PFO2HxA)	246.0	C ₄ HF ₇ O ₄	39492-88-1	3	6
perfluorooctanedioic acid (PFO3OA)	312.0	C ₅ HF ₉ O ₅	39492-89-2	4	8
perfluorodecandioic acid (PFO4DA)	378.1	C ₆ HF ₁₁ O ₆	39492-90-5	5	10

Table S2. Operational conditions of DWTP C on sampling day (August 18, 2014)

Parameter	Value
Raw water ozone dose	3.1 mg/L
Raw water total organic carbon concentration	6.0 mg/L
Aluminum sulfate coagulant dose	43 mg/L
Coagulation pH	5.70
Settled water ozone dose	1.3 mg/L
Settled water total organic carbon concentration	1.90 mg/L
Empty bed contact time in biological activated carbon filters	9.4 minutes for granular activated carbon layer 2.3 minutes for sand layer
Medium pressure UV dose	25 mJ/cm ²
Free chlorine dose	1.26 mg/L as Cl ₂
Free chlorine contact time	17.2 hours

Table S3. Water quality characteristics of surface water used in adsorption tests

Non-purgeable organic carbon (mg/L)	Ultraviolet absorbance at a wavelength of 254 nm	pH	Alkalinity (mg/L as CaCO ₃)	Conductivity (µS/cm)
9.036	0.399	7.53	19	133.5

Table S4. LC gradient method for PFAS analysis

Time (min)	Mobile Phase A % (v/v)	Mobile Phase B %	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mobile phase A: 2 mM ammonium acetate in ultrapure water with 5% methanol

Mobile phase B: 2 mM ammonium acetate in acetonitrile with 5% ultrapure water

Table S5. MS transitions for PFAS Analysis

Compound		MS/MS		Internal	
		Transition		standard	
Legacy PFASs	PFBA	212.8 → 168.8		13C4-PFBA	
	PFPeA	262.9 → 218.8		13C2-PFHxA	
	PFHxA	313.6 → 268.8		13C2-PFHxA	
	PFHpA	362.9 → 318.8		13C4-PFOA	
	PFOA	413.0 → 368.8		13C4-PFOA	
	PFNA	463.0 → 418.8		13C4-PFOA	
	PFDA	513.1 → 68.8		13C2-PFDA	
	PFBS	299.1 → 98.8		18O2-PFHxS	
	PFHxS	399.1 → 98.8		18O2-PFHxS	
	PFOS	498.9 → 98.8		13C4-PFOS	
PFECAs	PFMOAA	180.0 → 85.0		N/A	
	PFMOPrA	229.1 → 184.9		N/A	
	PFMOBA	279.0 → 234.8		N/A	
	PFPrOPrA	329.0 → 284.7		13C2-PFHxA	
	PFO2HxA	245.1 → 85.0		N/A	
	PFO3OA	311. → 84.9		N/A	
	PFO4DA	377.1 → 85.0		N/A	
	Perfluoro-n-[1,2,3,4- ¹³ C ₄]butanoic acid (13C4-PFBA)	217.0 → 172			
	Perfluoro-n-[1,2- ¹³ C ₂]hexanoic acid (13C2-PFHxA)	315.1 → 269.8			
	Perfluoro-n-[1,2,3,4- ¹³ C ₂]octanoic acid (13C4-PFOA)	417.0 → 372.0			
Internal standards	Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid (13C2-PFDA)	515.1 → 469.8			
	Sodium perfluoro-1-hexane[¹⁸ O ₂]sulfonate (18O2-PFHxS)	403.1 → 83.8			
Not applicable					

minimum, mean and median concentrations (ng/L) of PFASs at three drinking water intakes. *

Community A				Community B				Community C			
min	median	mean		min	median	mean		min	median	max	mean
<10	26	33	38	<10	12	12	104	<10	12	30	22
14	44	62	38	<10	19	19	116	<10	<10	<10	36
<10	48	78	42	<10	<10	<10	24	<10	<10	<10	<10
<10	39	67	85	<10	<10	<10	24	<10	<10	<10	<10
<10	34	46	32	<10	<10	<10	17	<10	<10	<10	<10
<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10	<10
<10	10	14	14	<10	<10	<10	14	<10	<10	<10	<10
<25	29	44	43	<25	<25	<25	40	<25	<25	<25	<25
<10	<10	<10	10	<10	<10	<10	4560	55	304	631	631
0	64	90	59	0	0	9	55	<10	<10	<10	<10
18	212	355	189	47	62	4696	55	345	710		

han quantitation limits were considered as zero to calculate means and Σ PFASs.

present in water samples from community C but could not be quantified and were therefore not included in

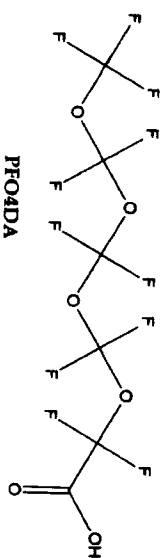
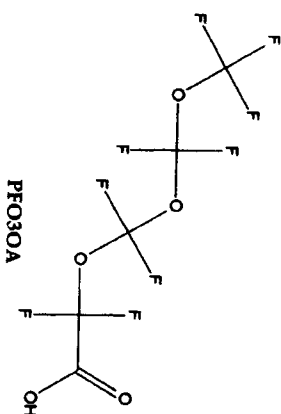
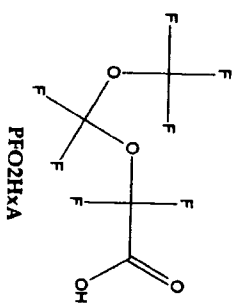
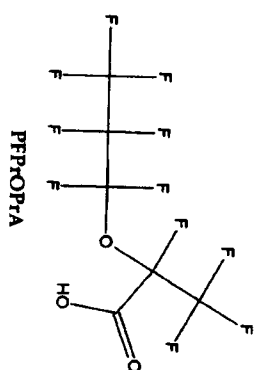
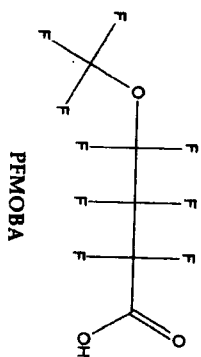
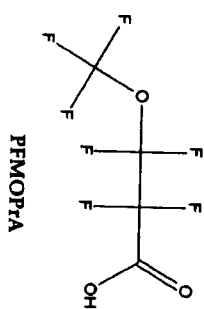
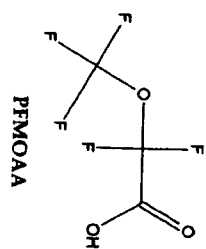


Figure S1. Molecular structures of PFECAs evaluated in this study

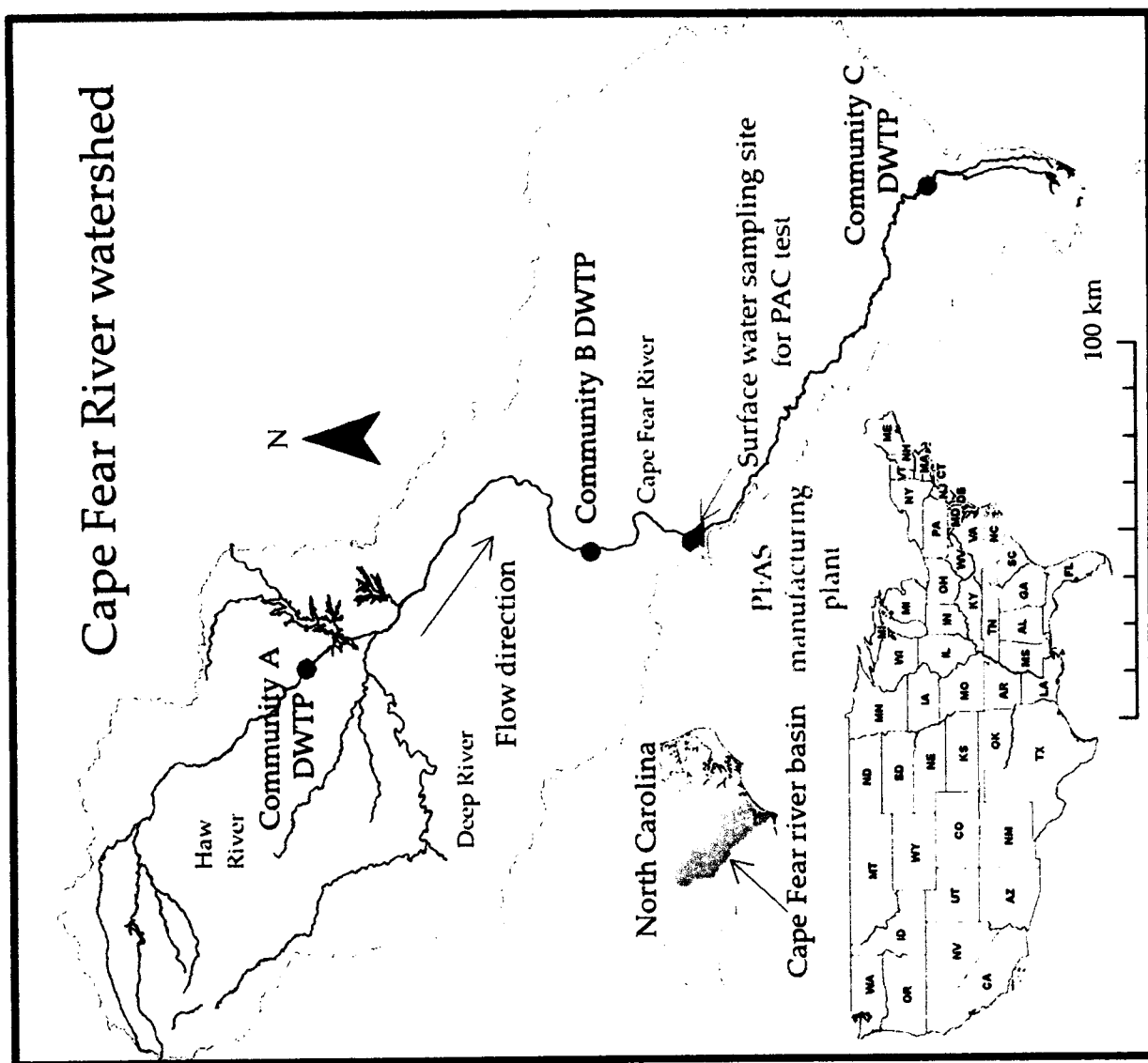
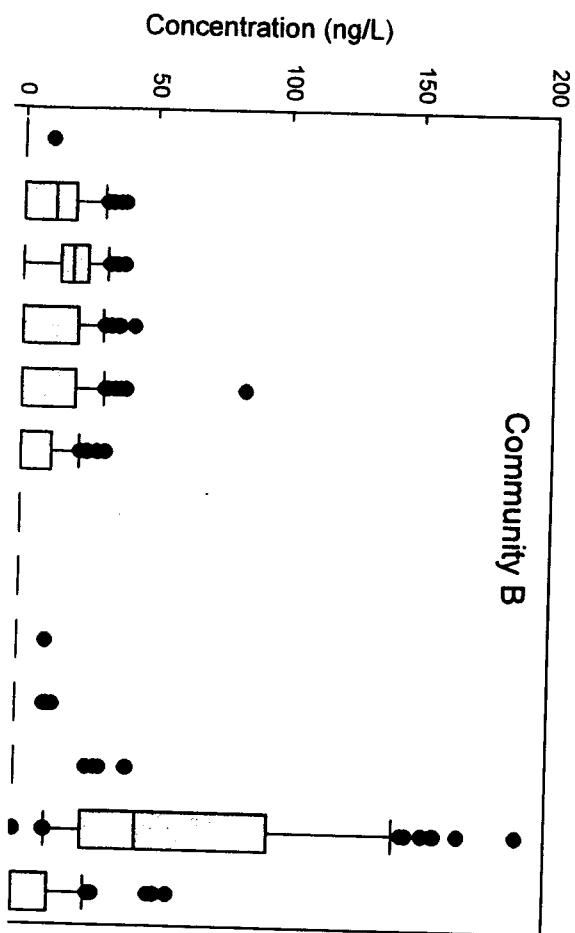
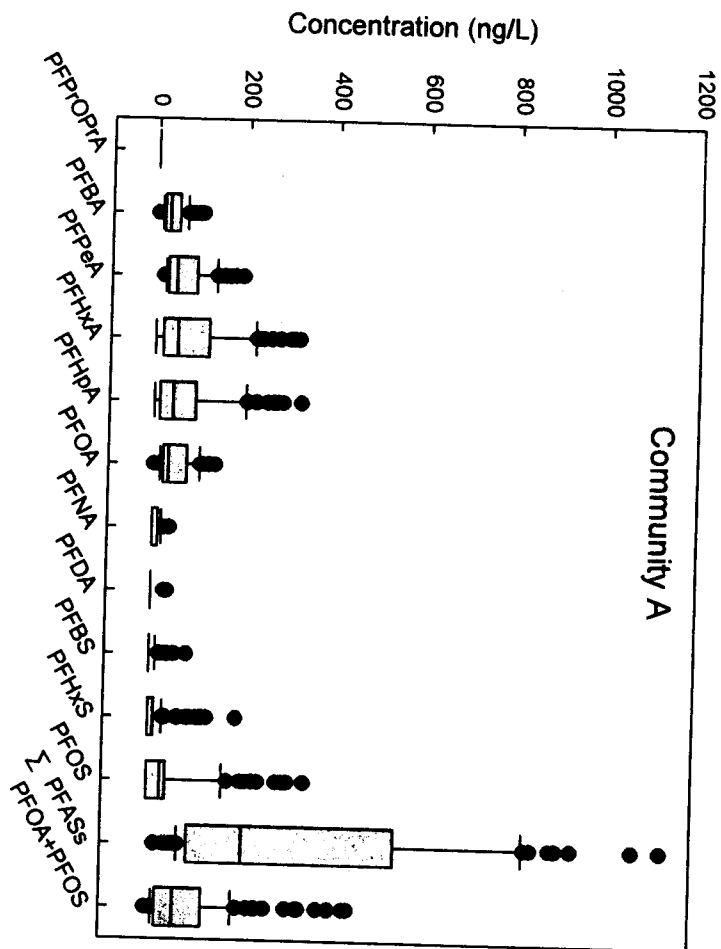


Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina. The scale is for the Cape Fear River watershed map.



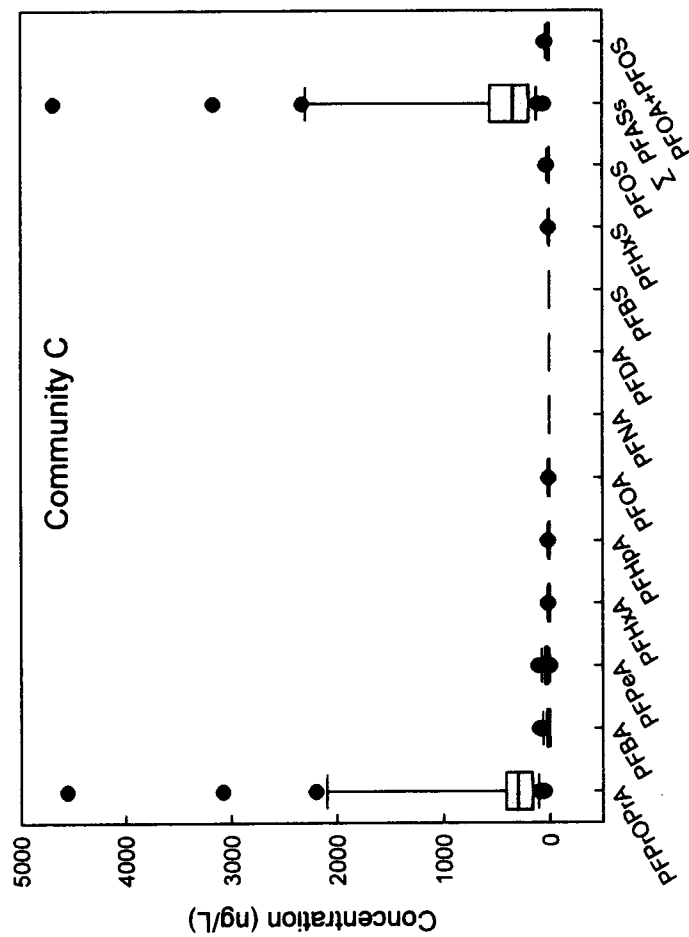
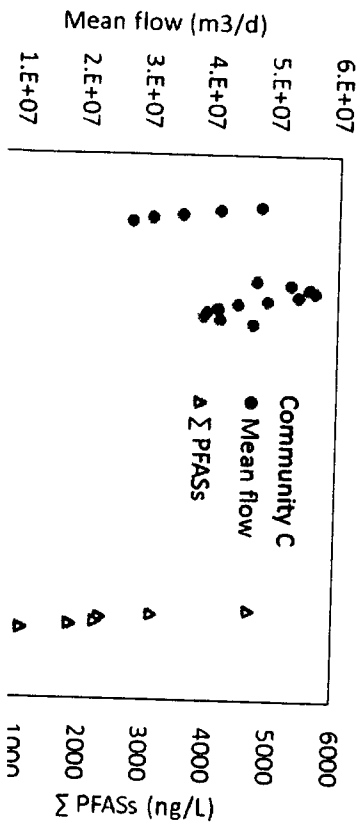
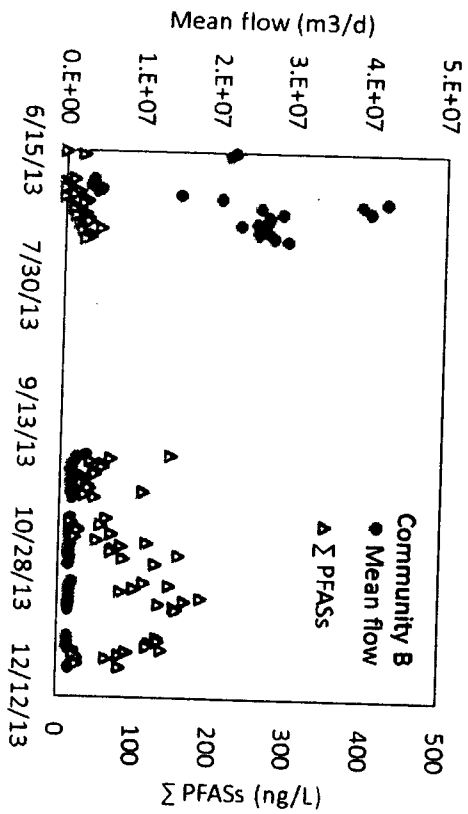
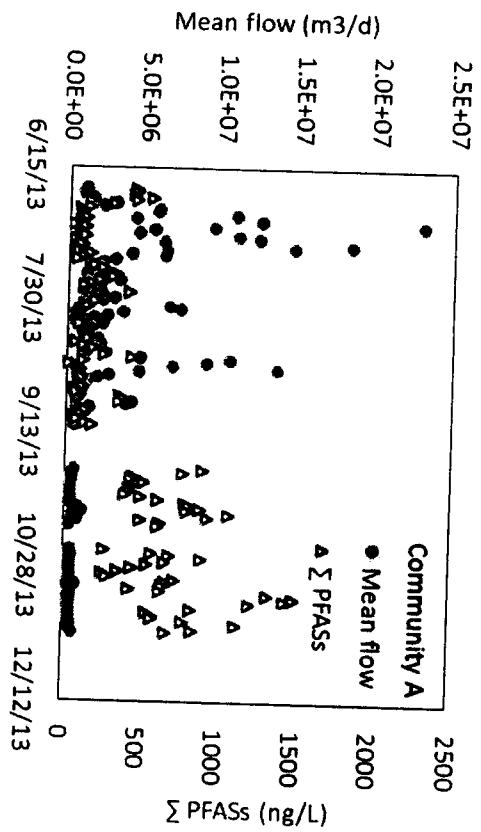


Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations less than quantitation limits were considered as zero. Upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; upper and lower bars represent the 90th and 10th percentile, respectively; and dots represent outliers (>90th or <10th percentile).



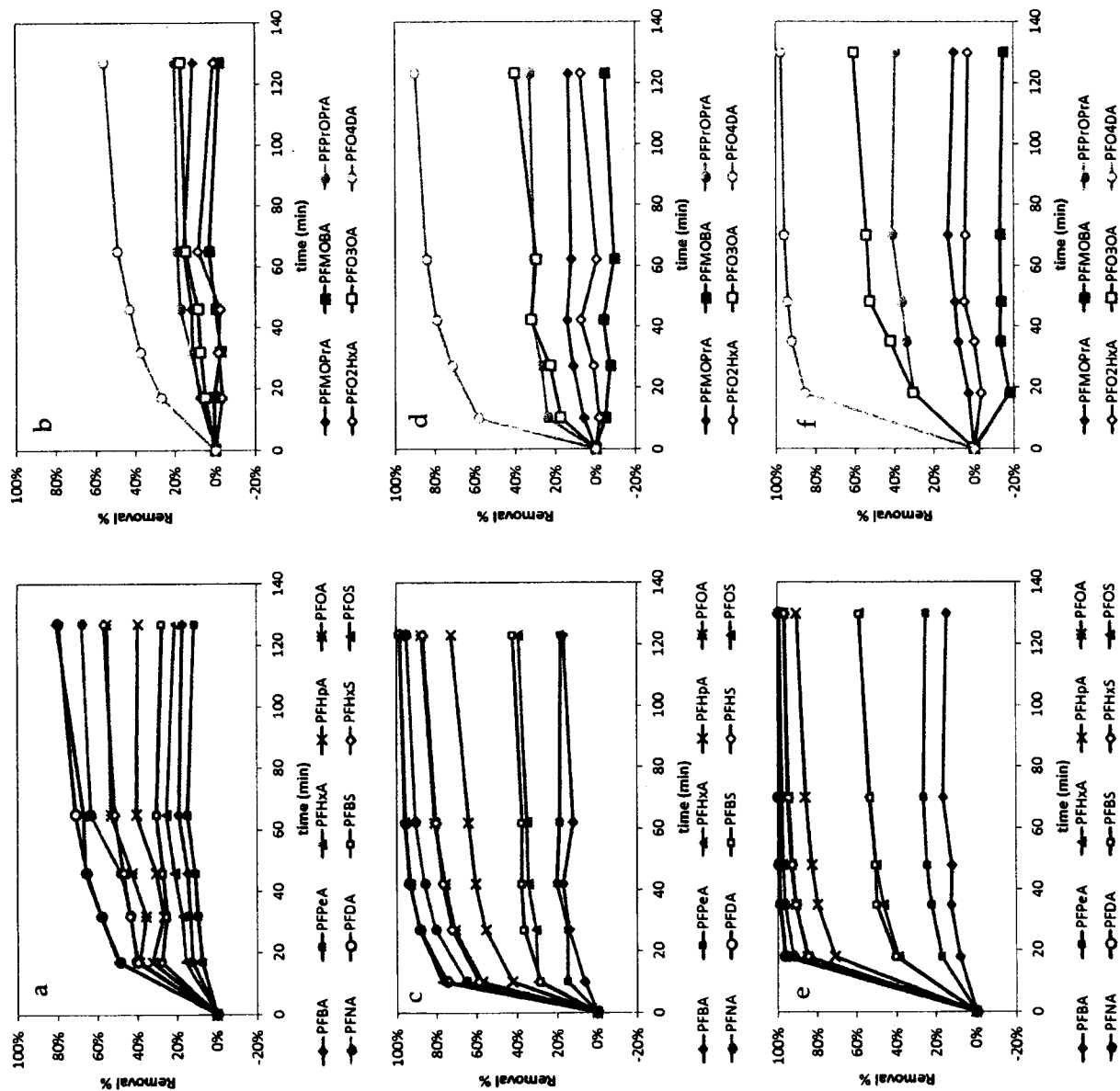


Figure S5. PFAS adsorption at powdered activated carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

Ben Kearns

From: Michael Richardson
Sent: Tuesday, May 3, 2016 2:57 PM
To: Ben Kearns
Subject: FW: Beginnings of a paper on perfluoroether carboxylic acids
Attachments: ESTL outline_0503.docx

FYI - Please review and let's discuss before I respond back the Dr. Knappe.

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, May 03, 2016 2:26 PM
To: Michael Richardson
Subject: Beginnings of a paper on perfluoroether carboxylic acids

Good afternoon, Mike,

I hope you are doing well. I wanted to share with you the beginnings of a paper we are writing on the occurrence of perfluoroalkyl substances, including the recently discovered perfluoroether carboxylic acids, in the Cape Fear River. The paper includes occurrence data at the intakes of three communities (labeled A, B, and C), including data at the Sweeney intake (community C). We are also including data to show the lack of removal of these compounds across unit processes at Sweeney. We would like to invite you as a co-author to recognize your contributions in collecting composite samples for us and providing us with the opportunity to collect samples at Sweeney. Could you review the attached and give me your feedback? Also, please let me know if you would like to be included as a co-author. In either case, we will keep you in the loop as we develop the paper further.

BTW, my new student Hillary Stoll is further developing the analytical method for these compounds and is planning to begin her sampling campaigns this summer for our current NSF project, on which you are a co-principal investigator. Once the semester winds down a bit, it would be good for us to come down to Wilmington, give you an update, and explore further sampling campaigns at your plant and in your distribution system.

Best,

Detlef

--
Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Ben Kearns

From: Michael Richardson
Sent: Thursday, August 11, 2016 11:42 AM
To: Mike McGill
Cc: Ben Kearns
Subject: RE: Harvard study response draft

I believe Ben has found a couple of minor detects in the 2014 data that I overlooked. Although minor in detection, still would be considered a detection.

From: Mike McGill
Sent: Thursday, August 11, 2016 9:58 AM
To: Michael Richardson; Ben Kearns
Subject: Harvard study response draft

Mike and Ben,

As discussed with Mike, I used the hex chrome statement we developed as the basis for the response to the Harvard study. Please correct wherever necessary.

Mike

First, it is important to point out that CFPUA has not detected the chemicals in question – PFASs – since 2013, when they were detected in minute amounts. DuPont, situated well upstream on the Cape Fear River from Wilmington, changed their use of the chemicals after concerns were detailed to the company. Almost certainly as a direct result, CFPUA has not detected PFASs since 2013.

PFASs (for polyfluoroalkyl and perfluoroalkyl substances) are listed by U.S. Environmental Protection Agency (EPA) as part of their **Unregulated Contaminant Monitoring Rule (UCMR 3)** published in 2012. UCMA 3 requires large water systems like CFPUA to monitor for contaminants that are not currently regulated and then report their data to the EPA. The data collected on the contaminants is to be used by the EPA to provide a basis for future regulatory actions to protect public health.

As stated earlier, CFPUA did monitor for the contaminants and found PFASs present in the finished water within its system in very minute amounts in 2013. The test results were provided to the EPA as required under the Rule. Because PFASs were not regulated by the EPA, no further action by CFPUA was required.

However, as stated earlier, CFPUA has not detected PFASs in our water since 2013. CFPUA will continue to provide information to NC DEQ and the EPA and work with the agencies to address any concerns that they identify.

Ben Kearns

From: Ben Kearns
Sent: Thursday, August 11, 2016 11:42 AM
To: Michael Richardson
Subject: RE: Harvard study response draft

The only items I found which may require a small adjustment to the below statement is the following:

- Entry Point to Distribution Sample at SWTP on 6/9/2014 – PFHpA – 0.012 ug/L
- Entry Point to Distribution Sample at SWTP on 9/8/2014 – PFHpA – 0.027 ug/L
 - (PFHpA = Perfluoroheptanoic Acid)
 - MRL = 0.01 ug/L

I am confirming the reason for the sampling that took place in 2014 with the lab.

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Mike McGill
Sent: Thursday, August 11, 2016 9:58 AM
To: Michael Richardson; Ben Kearns
Subject: Harvard study response draft

Mike and Ben,

As discussed with Mike, I used the hex chrome statement we developed as the basis for the response to the Harvard study. Please correct wherever necessary.

Mike

First, it is important to point out that CFPWA has not detected the chemicals in question – PFASs – since 2013, when they were detected in minute amounts. DuPont, situated well upstream on the Cape Fear River from Wilmington, changed their use of the chemicals after concerns were detailed to the company. Almost certainly as a direct result, CFPWA has not detected PFASs since 2013.

PFASs (for polyfluoroalkyl and perfluoroalkyl substances) are listed by U.S. Environmental Protection Agency (EPA) as part of their **Unregulated Contaminant Monitoring Rule (UCMR 3)** published in 2012. UCMA 3 requires large water systems like CFPUA to monitor for contaminants that are not currently regulated and then report their data to the EPA. The data collected on the contaminants is to be used by the EPA to provide a basis for future regulatory actions to protect public health.

As stated earlier, CFPUA did monitor for the contaminants and found PFASs present in the finished water within its system in very minute amounts in 2013. The test results were provided to the EPA as required under the Rule. Because PFASs were not regulated by the EPA, no further action by CFPUA was required.

However, as stated earlier, CFPUA has not detected PFASs in our water since 2013. CFPUA will continue to provide information to NC DEQ and the EPA and work with the agencies to address any concerns that they identify.

Ben Kearns

From: Mike McGill
Sent: Thursday, August 11, 2016 3:58 PM
To: Ben Kearns
Subject: FW: Harvard study response draft

I changed the "very minute" phrasing to the phrases below. Tell me if you likey.

First, it is important to point out that CFPUA has not detected the chemicals in question – PFASs – since 2014, when they were found in amounts just over the detect level. DuPont, situated well upstream on the Cape Fear River from Wilmington, changed their use of the chemicals after concerns were detailed to the company. Almost certainly as a direct result, CFPUA has not detected PFASs since 2014.

PFASs (for polyfluoroalkyl and perfluoroalkyl substances) are listed by U.S. Environmental Protection Agency (EPA) as part of their **Unregulated Contaminant Monitoring Rule (UCMR 3)** published in 2012. UCMA 3 requires large water systems like CFPUA to monitor for contaminants that are not currently regulated and then report their data to the EPA. The data collected on the contaminants is to be used by the EPA to provide a basis for future regulatory actions to protect public health.

As stated earlier, CFPUA did monitor for the contaminants and found only one type within the family of PFASs present in the finished water within its system in amounts just over the detect level in 2014. The test results were provided to the EPA as required under the Rule. Because PFASs were not regulated by the EPA, no further action by CFPUA was required.

However, as stated earlier, CFPUA has not detected PFASs in our water since 2014. CFPUA will continue to provide information to NC DEQ and the EPA and work with the agencies to address any concerns that they identify.

Ben Kearns

From: Mike McGill
Sent: Friday, August 12, 2016 8:12 AM
To: Jim Flechtner; Michael Richardson; Ben Kearns
Cc: Kristi Irick
Subject: Harvard study response

FYI, Fox News picked up this story yesterday, along with other outlets.

This is our back-pocket statement on the matter. It will not be used unless we are asked about the situation or unless we feel it is important to get out front of it based on customer calls.

Kristi, I've copied you because you could get calls. Your staff is more than welcome to send the customers to me.

Mike

First, it is important to point out that CFPUA has not detected the chemicals in question – PFASs – since 2014, when they were found in amounts just over the detect level. DuPont, situated well upstream on the Cape Fear River from Wilmington, changed their use of the chemicals after concerns were detailed to the company. Almost certainly as a direct result, CFPUA has not detected PFASs since 2014.

PFASs (for polyfluoroalkyl and perfluoroalkyl substances) are listed by U.S. Environmental Protection Agency (EPA) as part of their **Unregulated Contaminant Monitoring Rule (UCMR 3)** published in 2012. UCMA 3 requires large water systems like CFPUA to monitor for contaminants that are not currently regulated and then report their data to the EPA. The data collected on the contaminants is to be used by the EPA to provide a basis for future regulatory actions to protect public health.

As stated earlier, CFPUA did monitor for the contaminants and found only one type within the family of PFASs present in the finished water within its system in amounts just over the detect level in 2014. The test results were provided to the EPA as required under the Rule. Because PFASs were not regulated by the EPA, no further action by CFPUA was required.

However, as stated earlier, CFPUA has not detected PFASs in our water since 2014. CFPUA will continue to provide information to NC DEQ and the EPA and work with the agencies to address any concerns that they identify.

Ben Kearns

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Sunday, September 18, 2016 12:06 PM
To: Ben Kearns; Michael Richardson; Mick Noland; Chad Ham; Adam Pickett
Subject: Manuscript on perfluorinated compounds for your review
Attachments: ESTL_0918.docx; ESTL_SI_0918.docx

Gentlemen,

My research group and EPA colleagues at RTP have drafted the attached manuscript for submission to Environmental Science and Technology Letters. We plan to submit in the week of September 26. The manuscript includes occurrence data for perfluorinated compounds from each of your treatment plants (raw water quality data for all three, and process performance data and finished water quality for Sweeney in Wilmington). We do not name communities, but it would not be difficult for a reader to figure out the names of the three communities. Please let me know whether you have any comments by COB on 9/23.

Thank you,

Detlef

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

Ben Kearns

From: Ben Kearns
Sent: Sunday, September 25, 2016 10:50 AM
To: Detlef Knappe
Cc: Michael Richardson
Subject: Re: Paper draft

Hey Detlef,

I apologize for the late response. This week has been interesting with Mike packing up and his retirement festivities.

Yes, we would be grateful if you added us as co-authors. I do not have any comments on it at this time.

Regards,

Ben Kearns

Sent from my iPhone

> On Sep 24, 2016, at 8:03 PM, Detlef Knappe <knappe@ncsu.edu> wrote:

>

> Hi Ben and Mike,

>

> I hope you are having a good weekend. Do you have any comments and interest in co-authorship on the PFAS paper I sent you?

>

> Best,

>

> Detlef

>

>

> --

> Detlef Knappe

> Professor

> 319-E Mann Hall

> Department of Civil, Construction, and Environmental Engineering North

> Carolina State University Campus Box 7908 Raleigh, NC 27695-7908

>

> Phone: 919-515-8791

> Fax: 919-515-7908

> E-mail: knappe@ncsu.edu

> Web page: <http://knappelab.wordpress.ncsu.edu/>

>

Ben Kearns

From: Allyson Ridout
Sent: Friday, June 16, 2017 9:13 AM
To: Ben Kearns
Cc: Jill Deaney
Subject: FW: Sweeney sampling schedule

From: Jill Deaney
Sent: Monday, October 24, 2016 3:57 PM
To: Allyson Ridout <Allyson.Ridout@cfpua.org>; Crystal Callahan <Crystal.Callahan@cfpua.org>
Subject: Sweeney sampling schedule

Due to a new EPA Health Advisory Ben has asked we begin annual monitoring on the Sweeney Post (special) for EPA method 537. Crystal is going to order bottles to collect the sample in November. After that we should plan on collecting the sample in September. We can add this to the sampling schedule at the next sampling meeting.

Thanks

Jill Deaney
Cape Fear Public Utility Authority
Environmental Management Department
Laboratory Manager
jill.deaney@cfpua.org



Pace Analytical Services, LLC
9800 Kincey Ave. Suite 100
Huntersville, NC 28078
(704)875-9092

SAMPLE ANALYTE COUNT

Project: Sweeney Post-Special EPA 537
Pace Project No.: 92319027

Lab ID	Sample ID	Method	Analysts	Analytes Reported	Laboratory
92319027001	Sweeney WTP-Post Clear Well	EPA 537	WFH	8	PASI-O

11/8/16

REPORT OF LABORATORY ANALYSIS

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PROJECT NARRATIVE

Project: Sweeney Post-Special EPA 537
Pace Project No.: 92319027

Method: EPA 537
Description: 537 Perfluorinated Compounds
Client: Cape Fear Public Utility Authority-Compliance
Date: November 17, 2016

General Information:

1 sample was analyzed for EPA 537. All samples were received in acceptable condition with any exceptions noted below or on the chain-of custody and/or the sample condition upon receipt form (SCUR) attached at the end of this report.

Hold Time:

The samples were analyzed within the method required hold times with any exceptions noted below.

Sample Preparation:

The samples were prepared in accordance with EPA 537 with any exceptions noted below.

Initial Calibrations (Including MS Tune as applicable):

All criteria were within method requirements with any exceptions noted below.

Continuing Calibration:

All criteria were within method requirements with any exceptions noted below.

Surrogates:

All surrogates were within QC limits with any exceptions noted below.

Method Blank:

All analytes were below the report limit in the method blank, where applicable, with any exceptions noted below.

Laboratory Control Spike:

All laboratory control spike compounds were within QC limits with any exceptions noted below.

Matrix Spikes:

All percent recoveries and relative percent differences (RPDs) were within acceptance criteria with any exceptions noted below.

QC Batch: 331809

A matrix spike and/or matrix spike duplicate (MS/MSD) were performed on the following sample(s): 35276305001

M1: Matrix spike recovery exceeded QC limits. Batch accepted based on laboratory control sample (LCS) recovery.

- MS (Lab ID: 1774827)
 - Perfluorobutanesulfonic acid
 - Perfluoroheptanoic acid
 - Perfluorohexanesulfonic acid
 - Perfluorononanoic acid
 - Perfluorooctanesulfonic acid
 - Perfluorooctanoic acid
- MSD (Lab ID: 1774828)
 - Perfluorobutanesulfonic acid
 - Perfluoroheptanoic acid
 - Perfluorohexanesulfonic acid
 - Perfluorononanoic acid
 - Perfluorooctanesulfonic acid

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PROJECT NARRATIVE

Project: Sweeney Post-Special EPA 537
Pace Project No.: 92319027

Method: EPA 537
Description: 537 Perfluorinated Compounds
Client: Cape Fear Public Utility Authority-Compliance
Date: November 17, 2016

QC Batch: 331809

A matrix spike and/or matrix spike duplicate (MS/MSD) were performed on the following sample(s): 35278305001

M1: Matrix spike recovery exceeded QC limits. Batch accepted based on laboratory control sample (LCS) recovery.

- Perfluorooctanoic acid

Additional Comments:

Analyte Comments:

QC Batch: 331809

E: Analyte concentration exceeded the calibration range. The reported result is estimated.

- MS (Lab ID: 1774827)
 - Perfluorohexanesulfonic acid
 - Perfluorooctanesulfonic acid
- MSD (Lab ID: 1774828)
 - Perfluorohexanesulfonic acid
 - Perfluorooctanesulfonic acid

This data package has been reviewed for quality and completeness and is approved for release.

REPORT OF LABORATORY ANALYSIS

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ANALYTICAL RESULTS

Project: Sweeney Post-Special EPA 537
Pace Project No.: 92319027

Sample: Sweeney WTP-Post Clear Well Lab ID: 92319027001 Collected: 11/08/16 08:00 Received: 11/08/16 15:38 Matrix: Water

Parameters	Results	Units	Report Limit	DF	Prepared	Analyzed	CAS No.	Qual
537 Perfluorinated Compounds								
Analytical Method: EPA 537 Preparation Method: EPA 537								
Perfluorobutanesulfonic acid	ND	ug/L	0.090	1	11/11/16 18:45	11/17/16 04:30	375-73-5	
Perfluoroheptanoic acid	0.013	ug/L	0.010	1	11/11/16 18:45	11/17/16 04:30	375-85-9	
Perfluorohexanesulfonic acid	ND	ug/L	0.030	1	11/11/16 18:45	11/17/16 04:30	355-46-4	
Perfluorononanoic acid	ND	ug/L	0.020	1	11/11/16 18:45	11/17/16 04:30	375-95-1	
Perfluorooctanesulfonic acid	ND	ug/L	0.040	1	11/11/16 18:45	11/17/16 04:30	1763-23-1	
Perfluorooctanoic acid	0.013	ug/L	0.0020	1	11/11/16 18:45	11/17/16 04:30	335-67-1	
Surrogates								
Perfluorohexanoic acid (S)	92	%	70-130	1	11/11/16 18:45	11/17/16 04:30		
Perfluorodecanoic acid (S)	107	%	70-130	1	11/11/16 18:45	11/17/16 04:30		

REPORT OF LABORATORY ANALYSIS

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Date: 11/17/2016 07:53 PM

Ben Kearns

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Thursday, March 2, 2017 2:57 PM
To: Ben Kearns
Cc: Jill Deaney
Subject: Re: Perfluorinated chemicals in the Cape Fear River

Ben,

My schedule is quite flexible on Monday morning and again after 3 pm. It is our spring break :)

Best,

Detlef

On 3/2/17 1:28 PM, Ben Kearns wrote:

> Hello Detlef,

>

> I would love to discuss these compounds next week. I am available Monday/Tuesday throughout the day, Thursday before noon, and Friday noon till 5pm. Please let me know what date/time works best for you and we will set up a call.

>

> Regards,

>

>

> Ben Kearns

> Surface Water Operations Supervisor

> CFPUA Sweeney WTP

> 235 Government Center Drive

> Wilmington, NC 28403

> Office: 910-332-6577

> Cell: 910-398-4311

>

>

> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Thursday, March 02, 2017 8:13 AM

> To: Ben Kearns <Ben.Kearns@cfpua.org>

> Subject: Perfluorinated chemicals in the Cape Fear River

>

> Hi Ben,

>

> We keep finding very high levels of perfluorinated chemicals in the Cape Fear River downstream of the Chemours plant, and their concentrations remain high as they travel downstream to your intake. Also, these chemicals pass untouched through Sweeney. Do you have some time next week to discuss?

>

> Best,

>

> Detlef

>
>
> --
> Detlef Knappe
> Professor
> 319-E Mann Hall
> Department of Civil, Construction, and Environmental Engineering North
> Carolina State University Campus Box 7908 Raleigh, NC 27695-7908
>
> Phone: 919-515-8791
> Fax: 919-515-7908
> E-mail: knappe@ncsu.edu
> Web page: <http://knappelab.wordpress.ncsu.edu/>
>

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Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

Ben Kearns

From: Jill Deaney
Sent: Monday, March 06, 2017 10:05 AM
To: Ben Kearns
Cc: Jill Deaney; Allyson Ridout; Adam Poore
Subject: RE: Perfluorinated chemicals in the Cape Fear River

Ben,

Below is a summary of our detects for the Perfluorinated compounds which were analyzed using EPA method 537.

The first four samples were included in our UCMR3 monitoring.

Based on our results, in October 2016 we decided to begin special sampling on the Post CW with the first sample scheduled for November 2016 and then annually in September which was the month the results were the highest.

We have not tested our raw water to see if we have any removal so we could add the raw site to our annual sample.

Sample date	Sample location	Perfluoroheptanoic Acid (PFHpA) (µg/L)	Perfluorooctanoic acid (PFOA) (µg/L)
12/5/2013	Post CW	0.014	ND
3/11/2014	Post CW	ND	ND
6/9/2014	Post CW	0.012	ND
9/8/2014	Post CW	0.027	ND
11/8/2016	Post CW	0.013	0.013

Next test scheduled for Post CW for September 2017.

Jill

-----Original Message-----

From: Ben Kearns
Sent: Monday, March 06, 2017 9:20 AM
To: Jill Deaney <Jill.Deaney@cfpua.org>
Subject: RE: Perfluorinated chemicals in the Cape Fear River

No worries.

I wanted to simply make the opportunity available to you if you had questions you would like to ask Dr. Knappe. If you have any questions feel free to forward them to me and I will be sure and ask him. I thought that between the two of us we could make it a very productive and insightful conversation regarding these contaminants of emerging concern.

? how do we communicate this info when nobody knows about them.

Goal → Chemours facility discharging these compounds.

↳ looking @ building a stakeholder group to significantly ↓ the input of the chems.

(Sent message to NFA) → Done by 7/14 Dix + Greenville.

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,^{*,†,‡,§} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||} Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

[†]Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

[‡]Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[§]National Exposure Research Laboratory, U.S. Environmental Protection Agency Research, Triangle Park, North Carolina 27711, United States

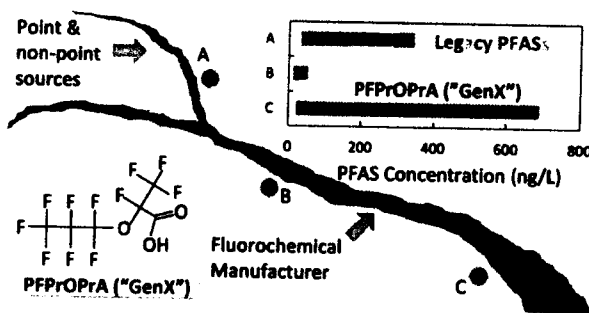
^{||}Cape Fear Public Utility Authority, Wilmington, North Carolina 28403, United States

[⊥]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECA were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n = 37$). Six other PFECA were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain perfluoroalkyl sulfonic acids [$\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$; $n \geq 6$ (PFSAs)] and perfluoroalkyl carboxylic acids [$\text{C}_n\text{F}_{2n+1}\text{COOH}$; $n \geq 7$ (PFCAs)] were predominantly used.² Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs^{3,4} has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health

advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.^{5,6} Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.^{7–10} Some fluorinated alternatives were recently identified,^{8,11} but others remain unknown^{12–14} because they are either proprietary or manufacturing byproducts.

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Revised: November 8, 2016

Accepted: November 10, 2016

Published: November 10, 2016

Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLS, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QLS. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.³² However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

Fate of PFASs in Conventional and Advanced Water Treatment Processes. To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.^{22–26} The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFASs, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.²⁵ Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400–500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2–113 times greater than that of PFPrOPrA (Figure 2b).

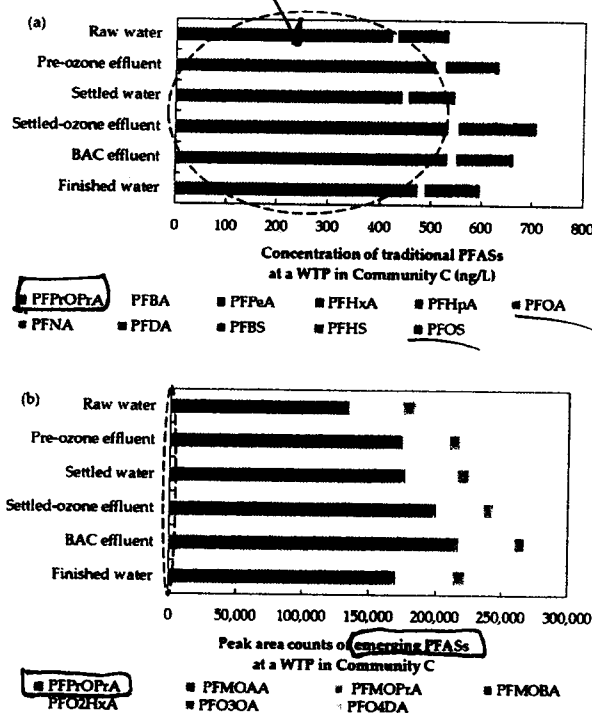


Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QLS were not plotted.

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

Adsorption of PFASs by PAC. PAC can effectively remove long-chain PFCAs and PFASs, but its effectiveness decreases with decreasing PFAS chain length.^{24,25,29} It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥ 7 . At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFASs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous

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- (28) Appleman, T. D.; Dickenson, E. R. V.; Bellona, C.; Higgins, C. P. Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids. *J. Hazard. Mater.* **2013**, *260*, 740–746.
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- (30) Dunn, S. E.; Knappe, D. R. U. *Disinfection by-product precursor and micropollutant removal by powdered activated carbon*; Water Research Foundation: Denver, 2013.
- (31) Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B. Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environ. Sci. Technol.* **2007**, *41* (15), 5271–5276.
- (32) Unregulated contaminant monitoring rule 3 (UCMR 3). <http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/>; U.S. Environmental Protection Agency: Washington, DC (accessed July 29, 2016).

Ben Kearns

From: Ben Kearns
Sent: Tuesday, March 28, 2017 8:39 PM
To: Jill Deaney
Subject: FW: Water Research Foundation RFP - Bromide and iodide
Attachments: RFP_4711.pdf

Hey Jill,

Please take a look at this and let me know if this is feasible for EMD staff to assist with. I will be reviewing the request and filtering it through the proper channels prior to agreement due to the current nature of the research request climate.

Thank you!

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, March 28, 2017 8:05 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Water Research Foundation RFP - Bromide and iodide

Hi Ben,

I am part of a team that is developing a proposal in response to the attached RFP entitled "Occurrence of bromide and iodide in water supplies"

We are currently recruiting utility participants for this study, in which we will be documenting bromide and iodide levels in drinking water sources across the US. We also plan to link the levels of bromide and iodide to disinfection byproduct formation.

We will be collecting samples on a quarterly basis for one year. Would you be willing to collect such samples and send them to the research team at the time you are collecting quarterly DBP compliance samples?

I am happy to provide more details. Sweeney participated in such an effort about 15 years ago. It would be a great opportunity to compare current levels to those found in the past.

Please let me know your thoughts.

Best,

Detlef

--

Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Ben Kearns

From: Ben Kearns
Sent: Thursday, April 13, 2017 9:19 AM
To: *Water Team* [Jim Flechtner; Frank Styers; Carel Vandermeiden; Jim Tayson; Elizabeth Severt; William Roy; Craig Wilson; Allyson Ridout; Overby, Tommy D; 'heidi.cox@ncdenr.gov'; Steve Mongeau; Gary McSmith; Mike McGill; Justin Maurice; Eric Hatcher; Beth Eckert; Rebecca Cramer; Maggie Butler; Phil Brower]
Cc: John Malone (John.Malone@cfpua.org); Jacqueline Valade; Kevin Denson; Ken Vogt
Subject: Water Team Meeting PFOS/PFOA Presentation by Detlef Knappe
Attachments: 14D and PFAS Fate.docx

Hello All,

I have been approached by Detlef Knappe with NC State regarding legacy and emerging PFAS compounds in our raw water and their fate once they have passed through the Sweeney WTP treatment regime. Due to their persistent nature and potential concentrations in our source water, there is a strong desire to identify the PFAS compounds, their concentrations, and their fate in our treatment plants through a coordinated sampling effort with Detlef's lab. I have attached a short proposal outlining the project scope and desired sampling for the group to review. The scope of this project is such that thorough vetting and buy-in from all Authority levels would be best before anything moves forward.

Detlef and a colleague who specialize in the study of these PFAS compounds have been invited to come to the next Water Team Meeting on **Wednesday, April 19th at 1:00pm** to give a short presentation for the group. I felt this would be a great opportunity for all parties involved to discuss the nature of these compounds, their source(s), and what options we have as a utility for removal with subject matter experts. I believe that as a progressive leader amongst the utilities in the area, our path forward regarding these PFAS compounds should be a collective decision made with the health and safety of our customers in mind.

I hope that all who are on this e-mail can attend and feel free to contact me with questions if you cannot attend.

Best Regards,

Mike McGill did not attend

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



Ben Kearns

From: Ben Kearns
Sent: Thursday, April 13, 2017 12:53 PM
To: Detlef Knappe
Subject: RE: Water Research Foundation RFP - Bromide and iodide

Hey Detlef,

Thank you for the proposal. I got it and forwarded it to our water team in preparation for the presentation next week. I did want to relay some initial comments from our executive team I received this morning at an early meeting. The decision regarding participation in the proposed research as well as PFAS curtailment efforts will not be decided upon in the Water Team Meeting. This will really need 1 or 2 smaller group meetings in order to make any decision regarding these items. They would like to hear about what these compounds are, how they relate to legacy PFAS, treatment/removal methods, and the scope and aim of the proposed research participation. Their main concern is CFPUA being singled out in the research and ringing too many "alarm bells" for items over which our control is limited.

There is definitely an interest in gaining more understanding of what we are dealing with in regards to PFAS and a desire to know the status of whether standard methods for these new compounds are available from third party labs.

We look forward to seeing you on Wednesday.

Best,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Thursday, April 13, 2017 12:42 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Water Research Foundation RFP - Bromide and iodide

Hi Ben,

I am part of a team that is developing a proposal in response to the attached RFP entitled "Occurrence of bromide and iodide in water supplies"

We are currently recruiting utility participants for this study, in which we will be documenting bromide and iodide levels in drinking water sources across the US. We also plan to link the levels of bromide and iodide to disinfection byproduct formation.

We will be collecting samples on a quarterly basis for one year. Would you be willing to collect such samples and send them to the research team at the time you are collecting quarterly DBP compliance samples?

I am happy to provide more details. Sweeney participated in such an effort about 15 years ago. It would be a great opportunity to compare current levels to those found in the past.

Please let me know your thoughts.

Best,

Detlef

P.S. Did you get my proposal I sent late last night?

--

Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

4-19-17

Perfluoroalkyl ether carboxylic acids: Occurrence in the Cape Fear river watershed and fate in drinking water treatment processes

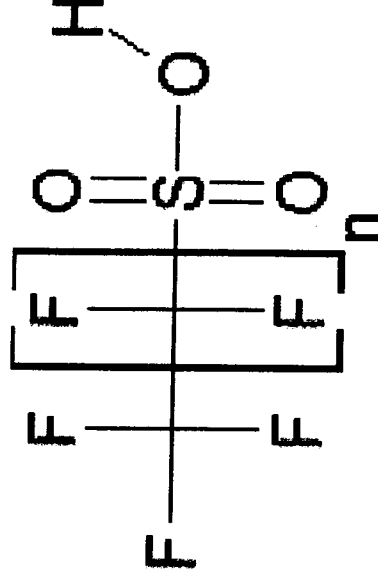
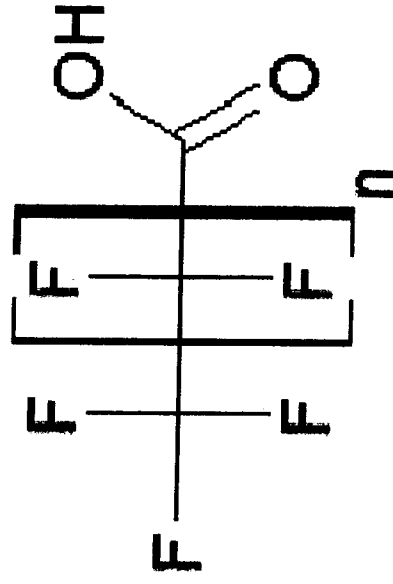
**Mei Sun, Elisa Arevalo, Leigh-Ann Dudley,
Andrew Lindstrom, Mark Strynar, Detlef Knappe**

NC STATE UNIVERSITY

Wilmington, April 19, 2017



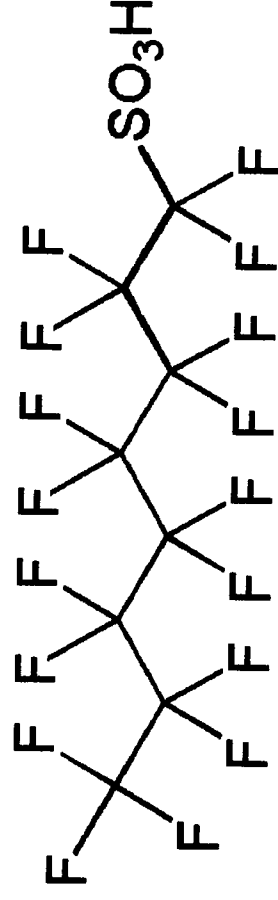
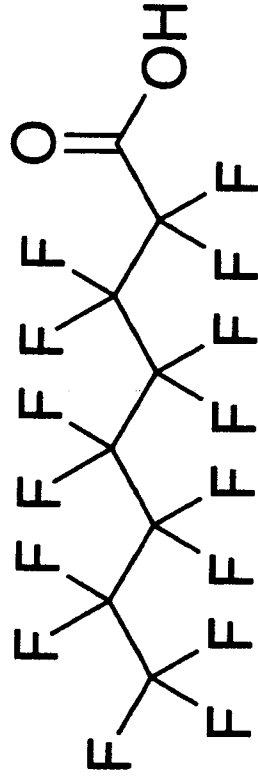
Perfluoroalkyl acids are organic compounds in which all C-H bonds are replaced with C-F bonds.



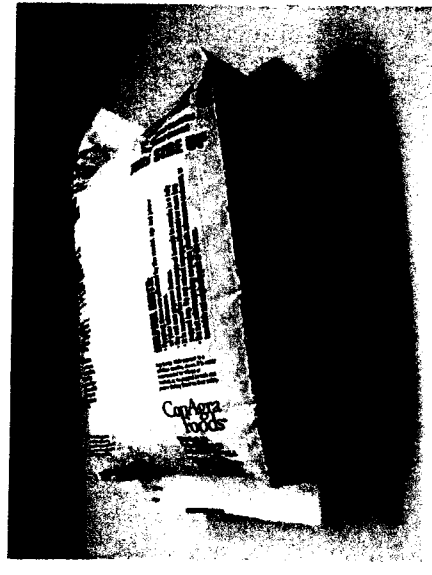
Long-chain PFASs:

PFCAs: $C_nF_{2n+1}COOH$, $n \geq 7$

PFSAs: $C_nF_{2n+1}SO_3H$, $n \geq 6$



Long-chain PFASs have long half-lives in humans



- Half-lives in humans

- PFOA: 3.8 years
- PFOS: 5.4 years
- PFBS: 4 months

- Toxicokinetic differences for PFOA

- 17-19 days in mice
- 4 hours in female rats



To protect the public from adverse health effects, health based guidelines have been established

EPA Health Advisory
(chronic exposure)



PFOS + C8:
70 ng/L

New Jersey

guidance level (C8)
and recommended
MCL (C9)




C8: 40 ng/L
C9: 13 ng/L

Are PFASs a concern in US drinking water?

Six PFASs were included in the third Unregulated Contaminant Monitoring Rule (UCMR3)

Compound	MRL (ng/L)
Perfluoroheptanoic acid (PFHpA, C7)	10
Perfluorooctanoic acid (PFOA, C8)	20
Perfluorononanoic acid (PFNA, C9)	20
Perfluorobutanesulfonic acid (PFBS)	90
Perfluorohexanesulfonic acid (PFHxS)	30
Perfluorooctanesulfonic acid (PFOS)	40



Samples collected from January 2013 – December 2015
Public Water Systems (PWSs) serving >10,000 people

At first glance, UCMR3 data suggest low PFAS detection frequency

UCMR3 requires monitoring for six PFASs in US drinking water. Monitoring began in 2013, and latest data release was January 2017.

PFAS	MRL (ng/L)	Occurrence (%)	Max. Concentration (ng/L)	Locations with high concentrations
C7	10	0.64	410	Saipan, PA, NY, DE, CO
C8	20	1.03	349	PA, MN, Saipan, DE, WV
C9	20	0.05	56	NJ, DE, PA, MA, NY
PFBS	90	0.05	370	GA, Saipan, CO, AL, PA
PFHxS	30	0.56	1,600	Saipan, AZ, DE, CO, PA
PFOS	40	0.79	7,000	Saipan, DE, CO, PA, WA

36,972 samples from 4,920 PWSs

PFAS detects: 599 samples (1.6%) from 198 PWSs (4.0%)

Of samples with PFAS detects: 23.4% derived from surface water

Some drinking water samples had PFOA+PFOS levels well above the HAL

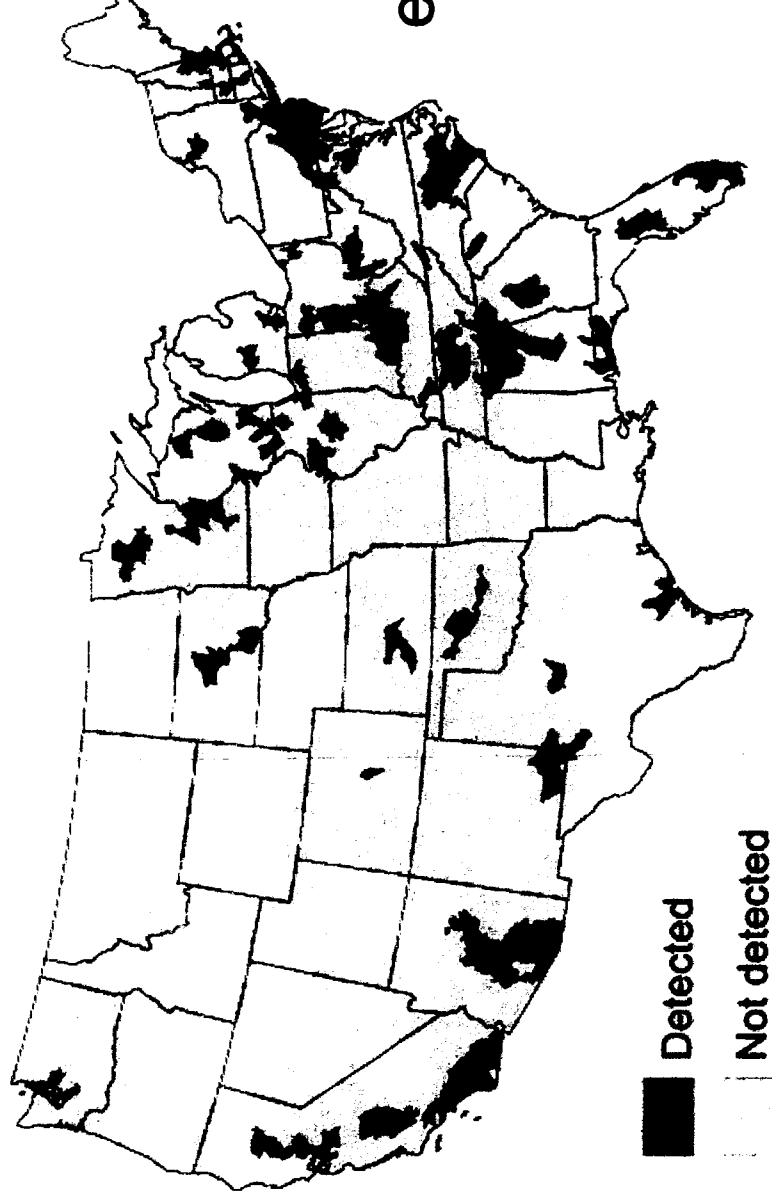
UCMR3 Data for North Carolina: PFAS detection frequency higher than for entire US

Compound	MRL (ng/L)	NC Detects
Perfluoroheptanoic acid (PFHpA, C7)	10	29 (max. 60 ng/L)
Perfluorooctanoic acid (PFOA, C8)	20	10 (max. 30 ng/L)
Perfluorononanoic acid (PFNA, C9)	20	0
Perfluorobutanesulfonic acid (PFBS)	90	0
Perfluorohexanesulfonic acid (PFHxS)	30	5 (max. 110 ng/L)
Perfluorooctanesulfonic acid (PFOS)	40	8 (max. 90 ng/L)

1,320 samples from 151 PWSs in NC
 PFAS detects: 43 samples (3.3%) from 20 PWSs (13.2%)
 Of samples with PFAS detects: 79% derived from surface water

Elevated PFAS levels affect a sizeable number of US residents

Hydrological units with detectable PFASs



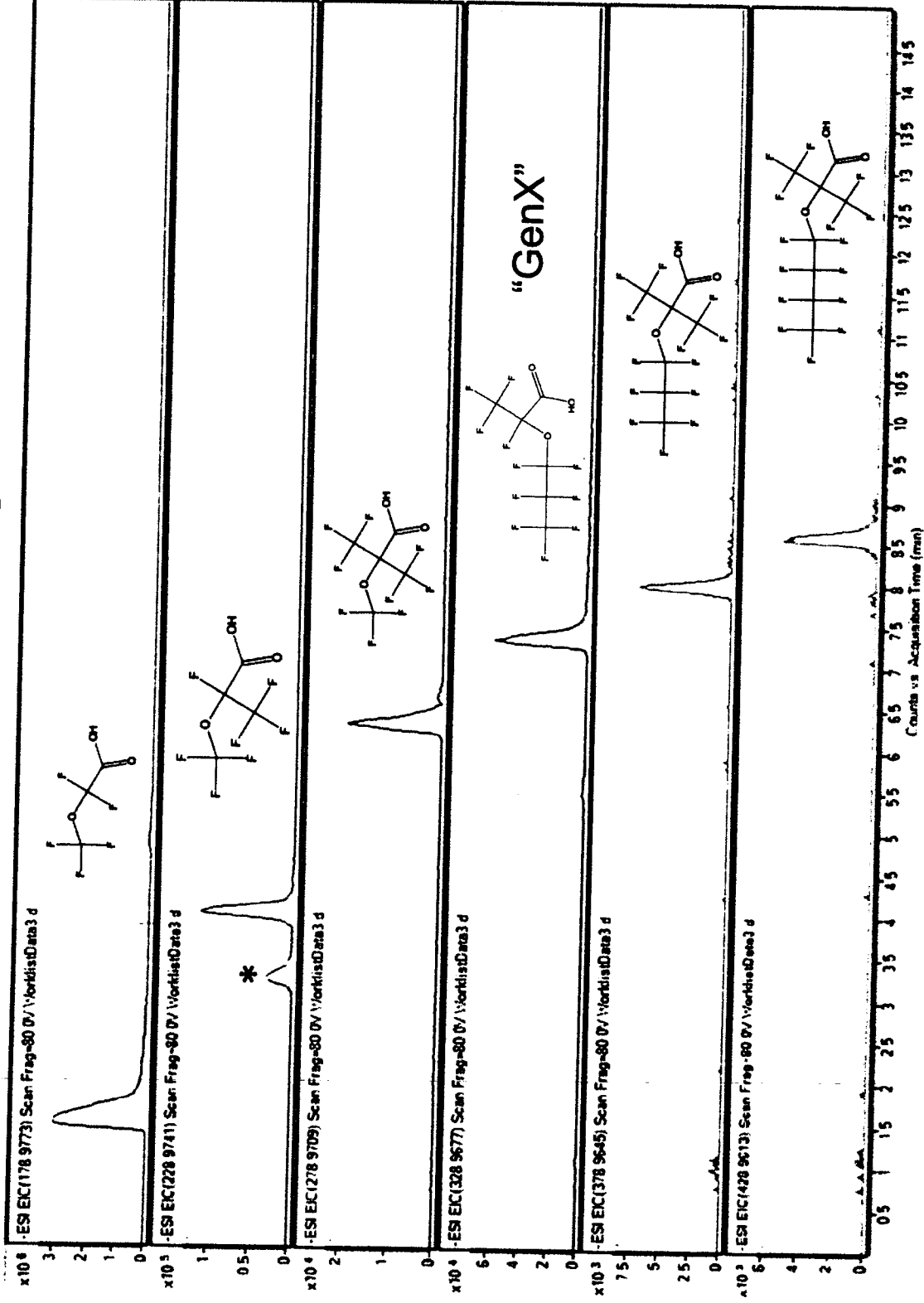
PFOS+PFOA levels estimated to exceed the 70 ng/L HAL in the drinking water of 6 million US residents

**...but are we
seeing the
complete picture?**

Many PFASs are used in commerce

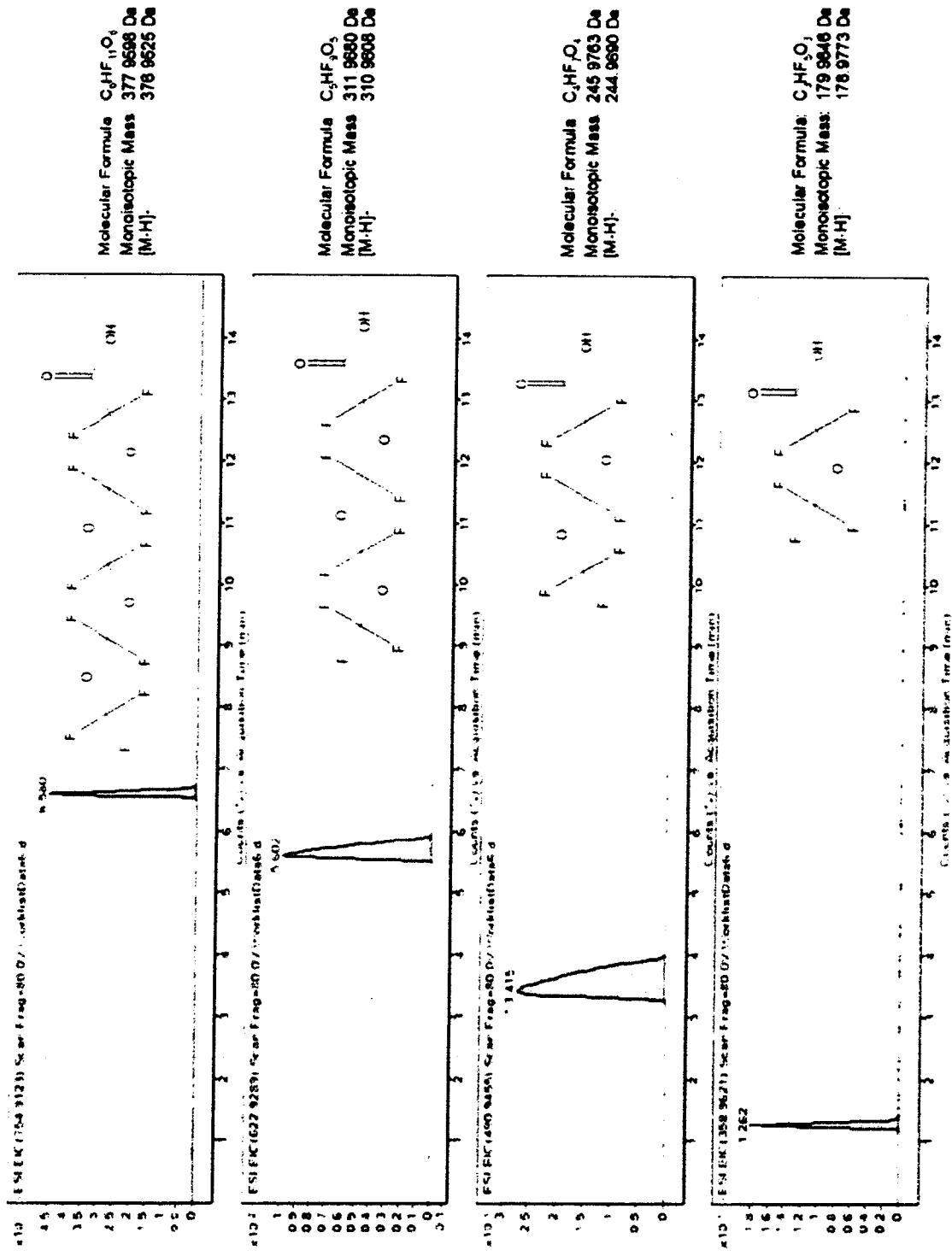
Sub-classes of PFASs	Examples of individual compounds*	Number of peer-reviewed articles since 2002**
perfluoroalkyl acids (PFAAs)	PFCAs $(C_nF_{2n+1}-COOH)$	<ul style="list-style-type: none"> PFBA (n=4) 928 PFPeA (n=5) 698 PFHxA (n=6) 1081 PFHpA (n=7) 1186 PFOA (n=8) 4066 PFNA (n=9) 1496 PFDA (n=10) 1407 PFUnA (n=11) 1069 PFDoA (n=12) 1016 PFTrA (n=13) 426 PFTeA (n=14) 587 PFBS (n=4) 654 PFHxS (n=6) 1081 PFOS (n=8) 3507 PFDS (n=10) 340
	PFSAs $(C_nF_{2n+1}-SO_3H)$	<ul style="list-style-type: none"> PFAPA (n=4) 3 PFHpPA (n=6) 33 PFOPA (n=8) 31 PFDPa (n=10) 35
	PFPAs $(C_nF_{2n+1}-PO_3H_2)$	<ul style="list-style-type: none"> C4/C4 PFPa (n=m=4) 4 C6/C6 PFPa (n=m=6) 12 C8/C8 PFPa (n=m=8) 12 C6/C8 PFPa (n=6 m=8) 8
	PFPIAs $(C_nF_{2n+1}-PO_2H-C_mF_{2m+1}-R)$	<ul style="list-style-type: none"> ADONA $(CF_3-O-CF_2-O-CH_2CF_2-COOH)$ 4 ADONA $(CF_3-O-CF_2-O-CH_2CF_2-COOH)$ 26 EEA $(CF_3-O-CF_2-O-CF_2-COOH)$ 6 F-538 $(Cl-C_6F_4-O-CF_2-SO_3H)$ 14 MeFBSA $(n=4, R=N(CH_3)H)$ 25 MeFOA $(n=8, R=N(CH_3)H)$ 134 EtFBSA $(n=4, R=N(CH_3)H)$ 7 EtFOA $(n=8, R=N(CH_3)H)$ 259 MeFBSE $(n=4, R=N(CH_3)C_2H_4OH)$ 24 MeFOSE $(n=8, R=N(CH_3)C_2H_4OH)$ 116 EtFBSE $(n=4, R=N(CH_3)C_2H_4OH)$ 4 EtFOSE $(n=8, R=N(CH_3)C_2H_4OH)$ 146 SampAP $[(C_6F_5)SO_2N(C_2H_5)C_2H_4O]_n-PO_3H_2$ 8 100s of others
PFASs $(C_nF_{2n+1}-R)$ > over 3000 PFASs may have been on the global market	PASf-based substances $(C_nF_{2n+1}-SO_2-R)$	<ul style="list-style-type: none"> 4,2 FTOH (n=4, R=OH) 106 6,2 FTOH (n=6, R=OH) 375 8,2 FTOH (n=8, R=OH) 412 10,2 FTOH (n=10, R=OH) 165 12,2 FTOH (n=12, R=OH) 42 6,2 diPAP $[(C_6F_5)C_2H_4O]_n-PO_3H_2$ 23 8,2 diPAP $[(C_6F_5)C_2H_4O]_n-PO_3H_2$ 25 100s of others
	fluorotelomer-based substances $(C_nF_{2n+1}-C_2H_4-R)$	<ul style="list-style-type: none"> polytetrafluoroethylene (PTFE) polyvinylidene fluoride (PVDF) fluorinated ethylene propylene (FEP) perfluoroalkoxy polymer (PFA)
PFAA precursors		
fluoropolymers		
others		

Two series of PFECAs were recently discovered in the Cape Fear River



Strynar et al. ES&T (2015)

Two series of PFECAs were recently discovered in the Cape Fear River

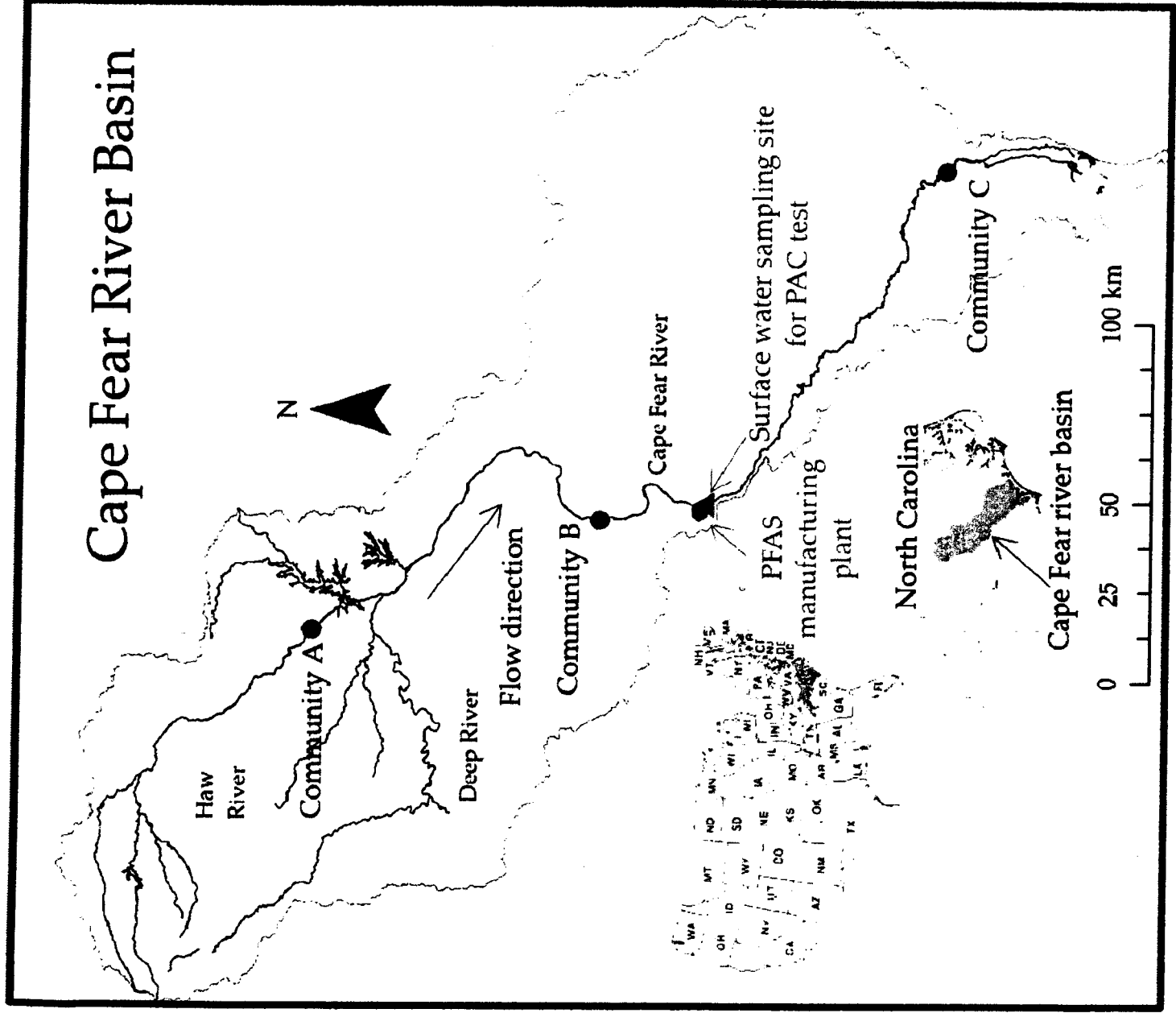


Strynar et al. ES&T (2015)

Study Design

Cape Fear River Basin

- Largest watershed in NC
- Supplies ~1.5M people with drinking water



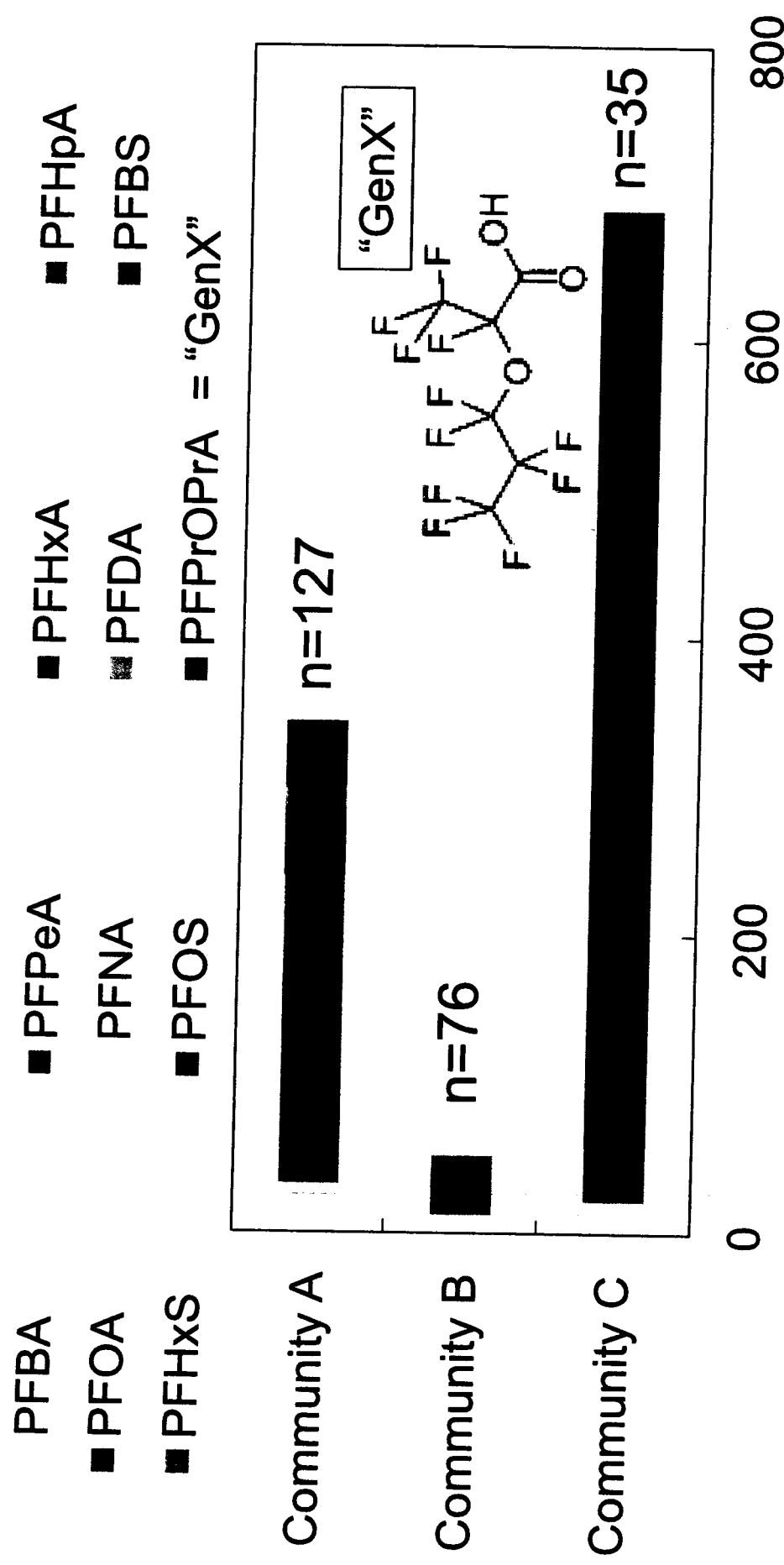
Sampling Protocol

- Samples collected in 1-L HDPE bottles
- Two sampling approaches
 - Daily composite samples of source water at three drinking water treatment plants
 - Grab samples to track PFAS fate in drinking water treatment plant
- No preservative
- Storage at room temperature
- Analysis within 7 days of sample collection

PFAS Analytical Method

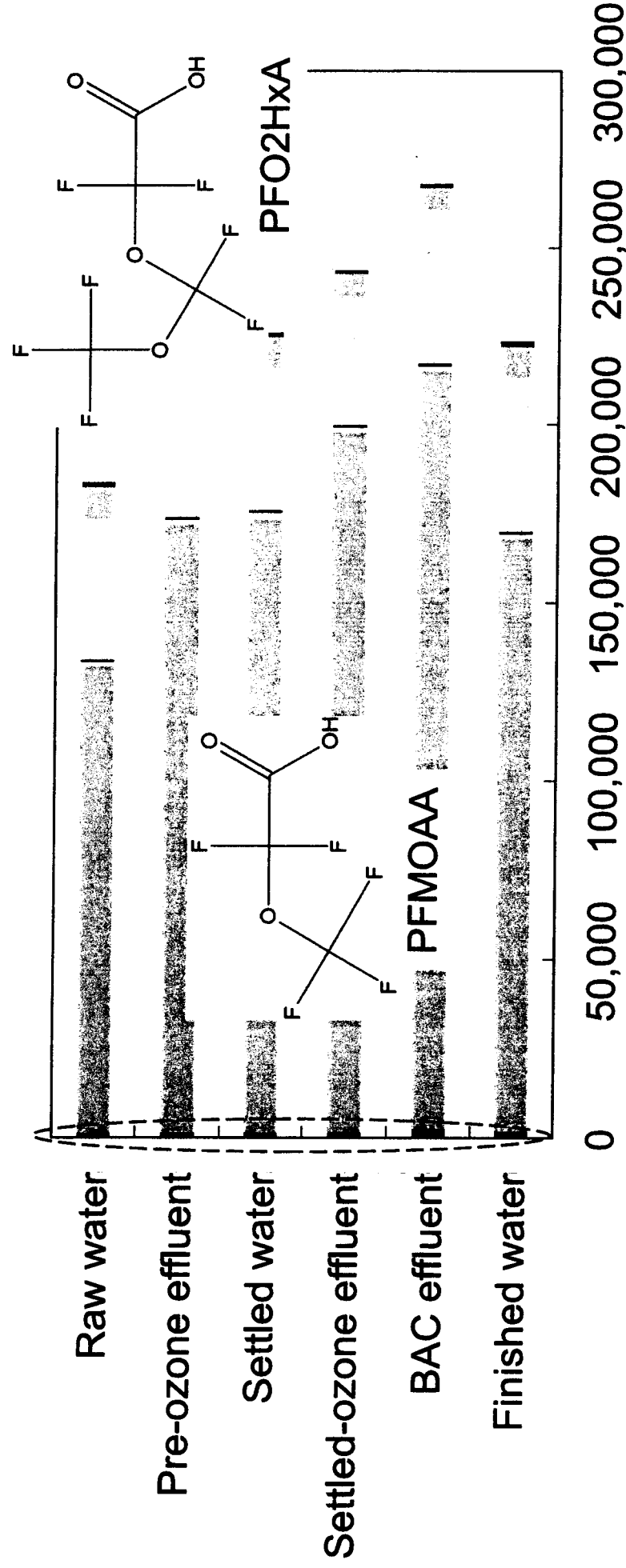
- PFAS concentrations measured by LC-MS/MS
- Large-volume direct injection (900 μL)
- Sample and standard preparation:
 - filtration with a 0.45- μm glass fiber filter
 - addition of mass-labeled internal standards
 - addition of formic acid
- Calibration curves ranged from 10 - 750 ng/L
- Limit of quantitation was 10 ng/L for all PFASs except C10 and PFOS (25 ng/L)

PFAS Occurrence in the CFR Watershed



Average concentration in drinking water source (ng/L)

Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX



Peak area counts of emerging PFASs at a WTP in Community C

■ PFPrOPrA ■ PFMOAA ■ PFMOPrA ■ PFMOBA ■ PFO2HxA ■ PFO3OA ■ PFO4DA

What about activated carbon?

PAC: thermally activated, wood-based

PAC Doses: 30, 60, 100 mg/L

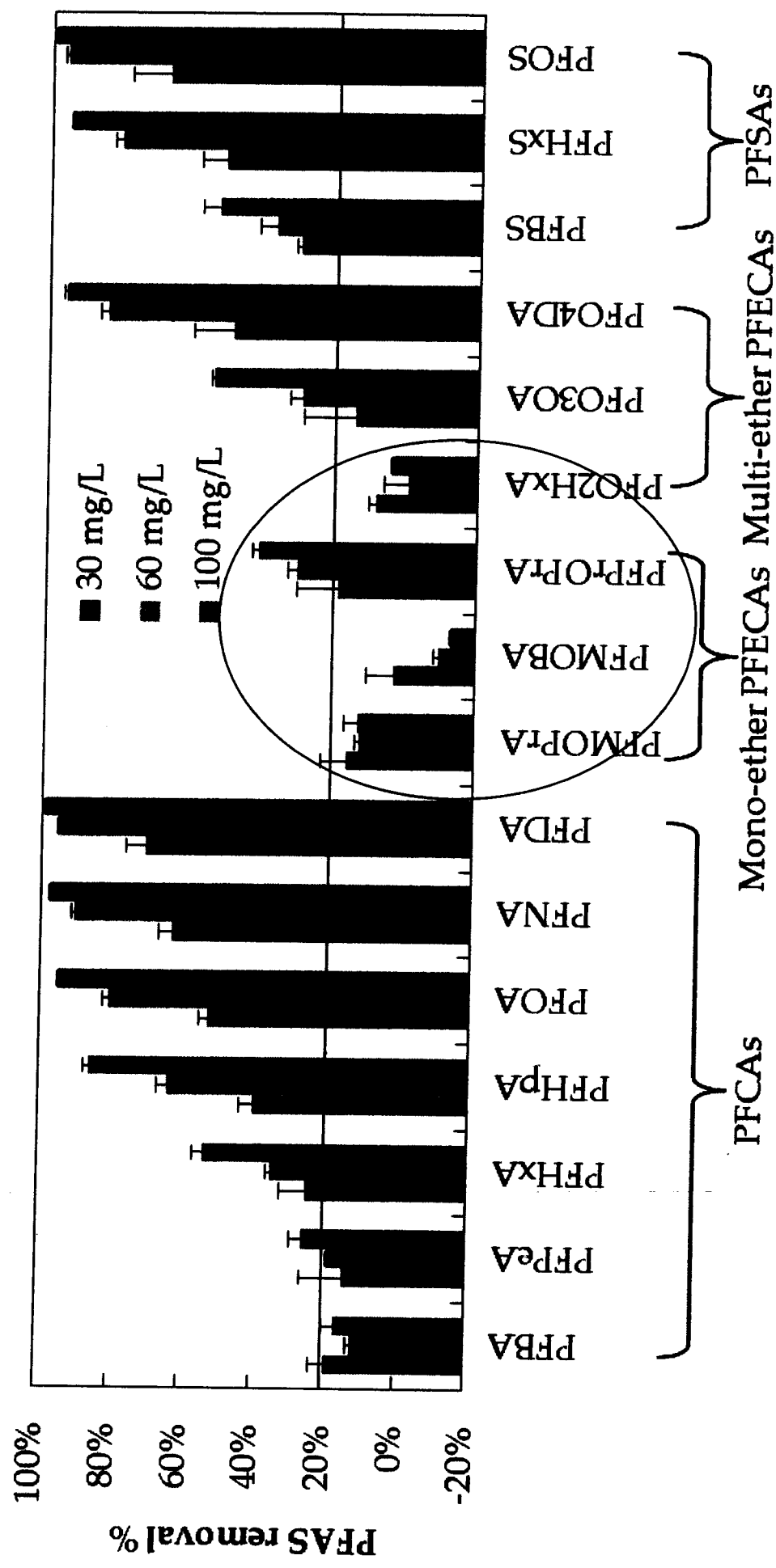
Contact time: 60 minutes

Water: Cape Fear River (TOC: 9.0 mg/L)

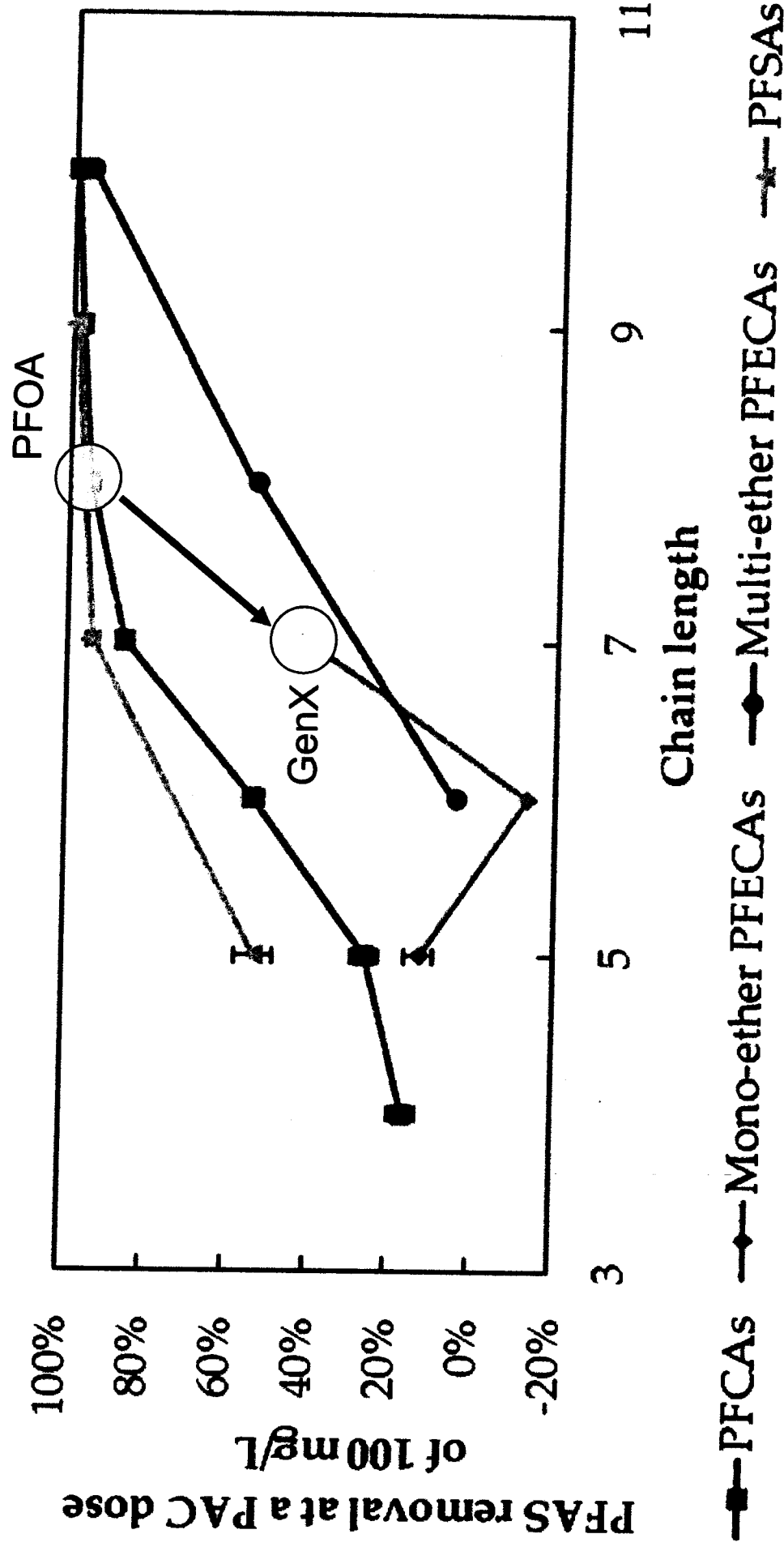
PFECAs: Native levels

PFCAAs and PFSAs: Spiked at 1000 ng/L

Adsorbability of PFASs varies greatly. The PFECAs that were present at the highest concentrations were essentially non-adsorbable



PFAS adsorbability: PFSA>PFCA>PFECA

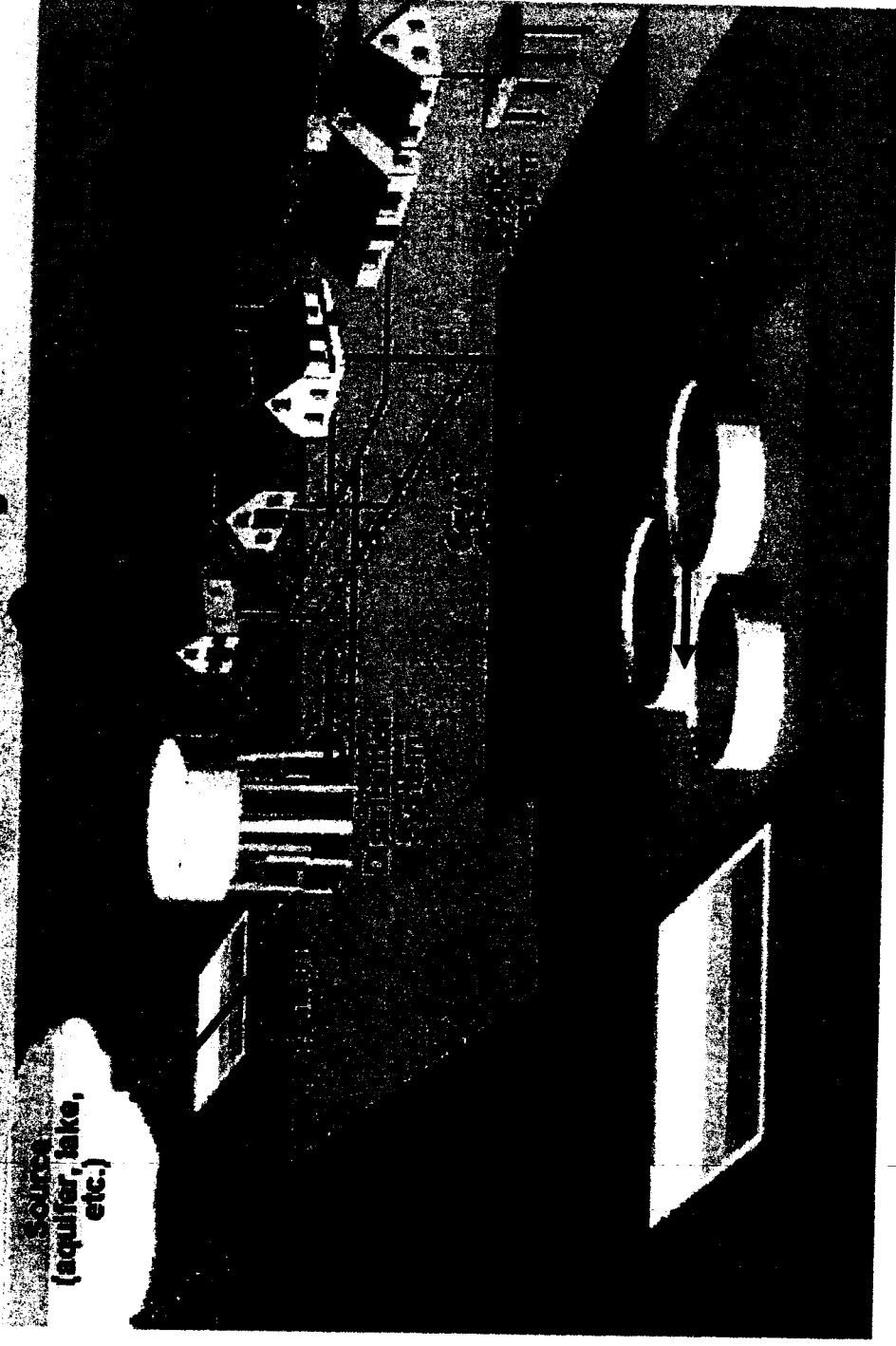


Proposed sampling plan

**1,4-Dioxane and PFAS Fate in
Urban Water Cycle**

Objective 1: Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle

The Drinking Water Cycle



Identify residence times/water ages at suitable sampling points to trace a parcel of water through the water/wastewater system

Objective 2: Determine fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR)

Sample monthly for one ASR cycle (ASR and monitoring wells)

- Recharge
- Storage
- Recovery

Laboratory	Biweekly	Monthly
Cape Fear Public Utilities Authority	Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge)	Total organic carbon, trihalomethanes
NCSU	Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride	1,4-dioxane, PFASs, dissolved organic carbon, UV ₂₅₄ absorbance

Objective 3: Determine possible association of 1,4-dioxane and PFASs with biosolids

Measure 1,4-dioxane and PFAS concentrations in aqueous and solid phases of biosolids. Determine partition coefficients.

Target Audiences for Results

- CFPUA staff
 - Data expected to illustrate treatment/ operational challenges associated with PFASs and 1,4-dioxane
 - Demonstrate need for source control – eliminate PFASs and 1,4-dioxane at upstream NPDES discharge locations
- North Carolina DEQ
 - Raise awareness about treatment challenges with emerging contaminants
 - Expand scope of current 1,4-dioxane working group to start looking at possibilities for controlling PFAS sources

Acknowledgments

- National Science Foundation (Award #1550222)
- North Carolina Urban Water Consortium
- Adam Pickett, Chris Smith, Michael Richardson,
Ben Kearns at participating utilities



Ben Kearns

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Saturday, April 22, 2017 10:22 AM
To: Ben Kearns
Subject: GenX Toxicity

Hi Ben,

I found the following abstract about GenX toxicity, which purports that GenX is more toxic than PFOA. GenX concentrations in Wilmington, Brunswick, and Pender greatly exceed the current health advisory level for PFOA. I think it is important that we push to dramatically reduce inputs of GenX and similar compounds into the Cape Fear River!

The work described below comes from one of the top PFAS research groups in the world (Ian Cousins at Stockholm University in Sweden).

Detlef

Comparing the potency in vivo of PFAS alternatives and their predecessors

Gomis Ferreira, Melissa Ines
Vestergren, Robin
Borg, Daniel
Cousins, Ian T.
(English)Manuscript (preprint) (Other academic)

Abstract [en]

Since the year 2000, a number of per- and polyfluoroalkyl substances (PFASs) have been introduced onto the market to replace long-chain perfluoroalkyl acids (e.g. perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)) and their respective precursors. The main rationale for this industrial transition is that the PFAS alternatives are less bioaccumulative and toxic than their predecessors. Here, we evaluated to what extent differences in toxicological effect thresholds for PFASs, expressed as an administered dose, were confounded by differences in their distribution and elimination kinetics. Increased liver weight was selected as the investigated endpoint based on the availability of sufficient toxicological and toxicokinetic data to enable a comparison of sub-chronic effects. Converting administered doses into equivalent serum and liver concentrations significantly reduced the variability in the dose-response curves for perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (GenX). The toxicity ranking using serum (PFNA>GenX>PFOA>PFHxA>PFBA) and liver (GenX>PFNA>PFOA>PFHxA>PFBA) concentrations also indicated that some PFAS alternatives may have a higher toxic potency than their predecessors when correcting for differences in toxicokinetics. For PFOS and perfluorobutane sulfonic acid (PFBS) the conversion from administered dose to serum concentration equivalents did not change the toxicity ranking which, however, could be due to the internal dose of PFBS being too low to allow a correct comparison. This study illustrates the importance of taking toxicokinetics/internal dose into account in substitution of hazardous chemicals for independent evaluation of bioaccumulation and toxicity criteria.

Keyword

PFOS, PFOA, PFAS alternatives, toxicokinetic model, potency, toxicity

National Category

Environmental Sciences

Research subject

Applied Environmental Science

Identifiers

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Ben Kearns

From: Beth Eckert
Sent: Thursday, April 27, 2017 11:50 AM
To: Frank Styers; Ben Kearns; Jill Deaney; John Malone; Allyson Ridout; Adam Poore
Subject: FW: Npdes permitted
Attachments: NC0003573 Ownership Change.pdf; Ownership Change 2015.docx; Cover Ltr 2015.docx; 3573-fact sheet-2011.pdf

Due to our interest in the discharge form Chemora. I asked Jim Gregson if I could get a copy of their permit and info. Attached is their information that he provided.

-----Original Message-----

From: Gregson, Jim [mailto:jim.gregson@ncdenr.gov]
Sent: Thursday, April 27, 2017 11:10 AM
To: Beth Eckert <Beth.Eckert@cfpua.org>
Subject: RE: Npdes permitted

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section Division of Water Resources Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
Jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405

Email correspondence to and from this address is subject to the North Carolina Public Records Law and may be disclosed to third parties.

-----Original Message-----

From: Beth Eckert [mailto:Beth.Eckert@cfpua.org]
Sent: Wednesday, April 26, 2017 8:24 AM
To: Gregson, Jim <jim.gregson@ncdenr.gov>
Subject: Npdes permitted

Hey Jim

There is a manufacturing plant, Chemora, that discharges via NPDES permit into the cape fear river between here and Fayetteville. Is this group in your area and if so can I get a copy of there permit?

Beth Eckert

Ben Kearns

From: Frank Styers
Sent: Monday, May 1, 2017 2:12 PM
To: Ben Kearns
Cc: John Malone; Beth Eckert
Subject: RE: perfluoroalkyl substances project

Ben,

Once you receive the additional information requested from Detlef, I would like to meet with you, Beth and John to review it. I'll be happy to schedule the meeting if you will let me know when you have the information.
Thanks

From: Ben Kearns
Sent: Monday, May 01, 2017 11:07 AM
To: Frank Styers <Frank.Styers@cfpua.org>
Subject: FW: perfluoroalkyl substances project

Hey Frank,

I just wanted to keep you up to date on the progress of the PFOS/PFOA Research Request from Detlef Knappe. I sent him the below request for additional information as we discussed in Water Team. Once this information has been furnished, I will forward it on to the executive team and set up a meeting to determine what level of participation we are willing to provide.

I'll keep you updated on any developments as I receive them.

Best,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Ben Kearns
Sent: Tuesday, April 25, 2017 9:59 AM
To: 'Detlef Knappe' <knappe@ncsu.edu>
Subject: RE: perfluoroalkyl substances and UCMR3

Hey Detlef,

Ben Kearns

From: Ben Kearns
Sent: Tuesday, May 16, 2017 10:31 AM
To: Beth Eckert
Cc: John Malone (John.Malone@cfpua.org)
Subject: FW: Fwd: GenX in the Cape Fear River watershed

Hey Beth,

The below was sent to me by Detlef regarding inquiry from a Wilmington StarNews reporter, Vaughn Hagerty. His questions are aimed at the PFAS study Detlef presented on in the water team meeting. I do not feel that we have an obligation to answer any questions of his at this time due to the fact that it was Detlef's research, but having a discussion regarding what response we may need to provide to a news story would be prudent.

Thank you,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, May 15, 2017 6:10 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Fwd: Fwd: GenX in the Cape Fear River watershed

Ben,
Please see below.
Detlef

My name is Vaughn Hagerty. I'm a journalist working on a story about PFASs, including GenX, in some drinking water systems in New Hanover and Brunswick counties. The story is for the Wilmington StarNews.

I came across "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina" and was hoping you could help provide some important information and clarification for the article.

My initial questions are:

The paper labels the water treatment plants as A, B, C, and identifies a "fluorochemical manufacturer" upstream from C. Is treatment plant C the Cape Fear Public Utility Authority and is the manufacturer the Chemours (formerly DuPont) plant in Fayetteville? And your sampling took place in 2013?

I may be misreading but the paper also seems to state that treatment plant C's filtration was ineffective at removing GenX, or might have actually increased the concentration somehow? And the finished water (fig. 2a) contained levels of GenX similar to that of raw water? Is all of that correct?

Has any subsequent sampling and testing occurred? If so, could you elaborate on it or point me to someone who can? Is there any reason to believe that GenX either is or isn't still present in water from the Cape Fear downstream from the DuPont plant?

What does all this mean for people in the community served by C? Are the state or federal governments looking into this at all?

Can you speak at all about any potential health concerns? The searches I've done so far indicate that while the amount of research available on the potential health risks of GenX is small, at least some of it suggests it may have problems similar to that posed by PFOA. Can you address that or point me to someone who can?

Are you aware of any pictures that might have been taken during the sample gathering or other parts of the process that we might be able to publish? I'm looking for ways to illustrate the story.

Is there anyone else in North Carolina (or elsewhere) I should be speaking with about this?

I would sincerely appreciate any time you could spare to help me get this information. Let me know if there's anything else I could provide that would facilitate that.

Regards,

Vaughn Hagerty

John Malone

From: Ben Kearns
Sent: Thursday, April 20, 2017 8:30 AM
To: Frank Styers; Beth Eckert; 'heidi.cox@ncdenr.gov'; Eric Hatcher; Jill Deaney; Phil Brower; Maggie Butler; Katherine Willis; Mike McGill; Justin Maurice; John Malone; Jacqueline Valade; Jim Tayson
Cc: Kevin Denson; Allyson Ridout
Subject: FW: Water Team PFAS Presentation attached
Attachments: PFAS_Wilmington_041917.pdf

lab. coord.
Water Samples.

Hello All,

Thank you for attending the water team meeting yesterday and allowing Detlef to present and field questions on the emerging contaminants of PFOS/PFOA & PFAS. Attached you will find the presentation from yesterday and feel free to share with those staff who you feel would benefit.

Best,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Wednesday, April 19, 2017 2:52 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Presentation attached

Hi Ben,

Please see attached. Feel free to share with your staff.

Thank you,

Detlef

Detlef Knappe
Professor
19-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

TO: Ben Kearns
FROM: Detlef Knappe
SUBJECT: Fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle
DATE: April 12, 2017

Objective: Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle by tracing parcels of water through

- (1) The Sweeney water treatment plant
- (2) Wilmington's drinking water distribution system
- (3) Wilmington's sewage collection system
- (4) Wilmington's wastewater treatment plant

In addition, we are interested in evaluating the fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR) as well as association of 1,4-dioxane and PFASs with biosolids.

Audience:

- (1) CFPUA staff: provide data demonstrating treatment challenges associated with emerging contaminants that occur at elevated levels in the Cape Fear River at Wilmington's drinking water intake. This information can be useful in efforts to control industrial sources of pollution upstream of Wilmington's drinking water intake.
- (2) Department of Environmental Quality staff: Since 2015, we have informed DEQ staff about the presence of contaminants in the Cape Fear River basin. Our goal is to encourage DEQ staff to control sources of pollution that affect downstream drinking water providers.

Background: Several unregulated contaminants occur at elevated levels in the Cape Fear River and its head waters (Haw and Deep Rivers). Among the constituents of concern are bromide, a disinfection by-product precursor, 1,4-dioxane, a likely human carcinogen, and perfluoroalkyl substances (PFASs) that are associated with a variety of adverse health outcomes, including cancer. The proposed study will focus on PFASs and 1,4-dioxane. The USEPA recently established a health advisory level for two PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), at 70 ng/L. While PFOA and PFOS levels at Wilmington's drinking water intake are low, the concentration of GenX, a replacement for PFOA, is in the 100s of ng/L. In addition, several other PFASs are present at even higher concentrations (Sun et al. 2016a). In addition, 1,4-dioxane occurs in Wilmington's source water at levels that exceed the North Carolina's stream water quality standard of 0.35 µg/L. Ozonation can indirectly oxidize 1,4-dioxane via the generation of hydroxyl radicals (Knappe et al. 2017). In previous sampling campaigns, we established that the ozonation processes at the Sweeney WTP are capable of oxidizing approximately two-thirds of the 1,4-dioxane coming into the plant (Knappe et al. 2017). In contrast, PFASs appear to pass through the Sweeney WTP without measurable attenuation (Sun et al. 2016a). In the previous sampling campaigns, we did not take into account hydraulic residence time such that we were not tracing the same parcel of water through the plant. Also, we did not establish 1,4-dioxane and PFAS fate once water leaves the Sweeney WTP.

Approach: To determine the fate of 1,4-dioxane and PFAS in Wilmington's urban water cycle, a PhD student supported by our National Science Foundation grant will work closely with CFPUA staff to track parcels of water through the Sweeney WTP, through Wilmington's drinking water distribution system, through Wilmington's sewage collection system, and Wilmington's wastewater treatment plant. We are already quite familiar with the Sweeney WTP, where we propose to take samples at the following locations:

- (1) Raw water intake,
- (2) Effluent of pre-ozone reactor,
- (3) Effluent of settling basin,
- (4) Effluent of settled water ozone reactor,
- (5) Effluent of GAC biofilter,
- (6) Effluent of UV reactor, and
- (7) Point-of-entry (POE) to distribution system (following contact with free chlorine)

We would need help from CFPUA staff to identify suitable sampling points in the drinking water distribution and sewage collection systems, and to estimate water ages at these sampling points. This information will be used to develop a sampling plan that permits tracking of water parcels through Wilmington's urban water cycle. Once the sampling plan is finalized, the PhD student, with support of a CFPUA staff member, will collect water samples at the locations and time points identified in the sampling plan. Samples for 1,4-dioxane analysis will be collected in 500-mL wide-mouth brown glass bottles according to EPA method 522 and stored at 4C until analysis. Samples for PFAS analysis will be collected in 1-L HDPE bottles and stored at room temperature until analysis.

In addition, we are interested in assessing the fate of 1,4-dioxane and PFASs in Wilmington's ASR system. Based on our understanding of Wilmington's ASR system, typical operation involves recharge of treated drinking water from Oct./Nov. through March, storage from March through June, and recovery from July through September. We propose to collect samples at the ASR well and at monitoring wells located 300, 450, 800, and 1,400 feet away from the ASR well. One option is to take monthly samples to determine concentrations of 1,4-dioxane and PFASs only. Another option, based on discussions we had with CFPUA 2.5 years ago, would be to conduct a more extensive study. In that case, the water quality (WQ) parameters shown in Table 1 could be monitored in the recharge water, during storage in the Upper Peedee aquifer, and during recovery. As indicated in Table 1, some WQ parameters will be monitored biweekly and others monthly, and analyses would be shared between CFPUA and NCSU as indicated in Table 1.

Table 1. Water quality monitoring parameters

Laboratory	Biweekly	Monthly
Cape Fear Public Utilities Authority	Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge)	Total organic carbon, trihalomethanes
NCSU	Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride	1,4-dioxane, PFASs, dissolved organic carbon, UV ₂₅₄ absorbance

The monitoring results will illustrate to what extent 1,4-dioxane and PFAS concentrations (and also trihalomethanes) are attenuated during aquifer storage. Fluoride concentrations will be used as a tracer to quantify the extent of 1,4-dioxane and PFAS attenuation by dilution of recharge water with native groundwater. If attenuation occurs beyond that attributable to dilution, it will be related to redox conditions by measuring such parameters as redox potential, dissolved oxygen, nitrate, nitrite, ammonium, and sulfate.

Finally, we are interested in determining the partitioning of 1,4-dioxane and PFASs to biosolids. Currently, we are not familiar with the solids handling facilities at CFPUA's wastewater treatment plants. We would be looking for biosolids samples designated for land application. For the biosolids samples, we would measure 1,4-dioxane and PFAS concentrations in both the aqueous and solid phases. To accomplish this goal, we will separate the solids from the aqueous phase by centrifugation. The aqueous phase samples will be analyzed like any other water samples. The solid phase will be extracted with a 60/40 blend of acetonitrile/water (Washington et al. 2010), and we will measure 1,4-dioxane and PFAS levels in the solvent extracts. These two measurements will allow us to calculate partition coefficients describing the sorption of 1,4-dioxane and PFASs from water to biosolids.

Analytical methods

1,4-Dioxane concentrations will be determined by a recently developed GC/MS method in our laboratory (Sun et al. 2016b). PFAS concentrations will be determined by a LC-MS/MS method that targets approximately 20 PFASs, including perfluoroalkyl ether carboxylic acids that occur at high levels in Wilmington's source water (Sun et al. 2016a).

TOC/DOC will be measured by high-temperature combustion (Shimadzu TOC-VSCN analyzer) according to Standard Method 5310B. The concentration of UV-absorbing organic constituents will be measured at

a wavelength of 254 nm according to Standard Method 5910. Anion concentrations will be measured by ion chromatography using existing methods. NH_4^+ will be measured by colorimetric methods (Hach).

References

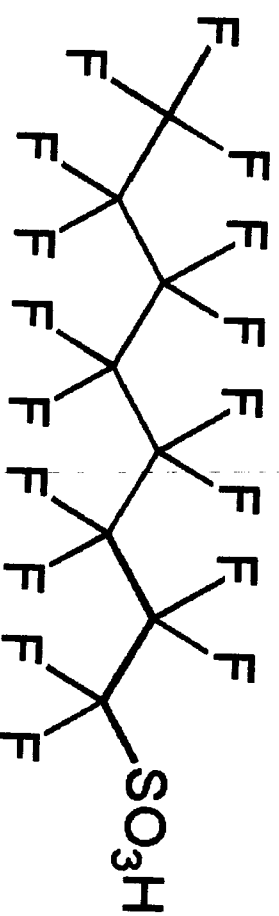
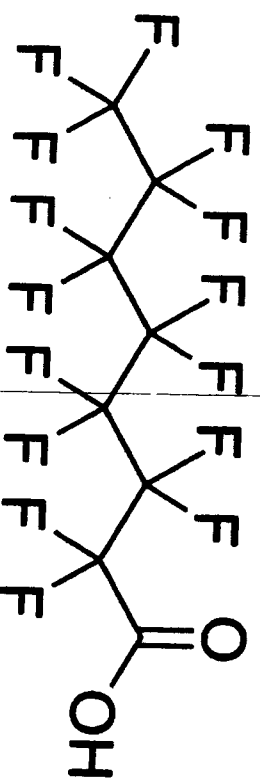
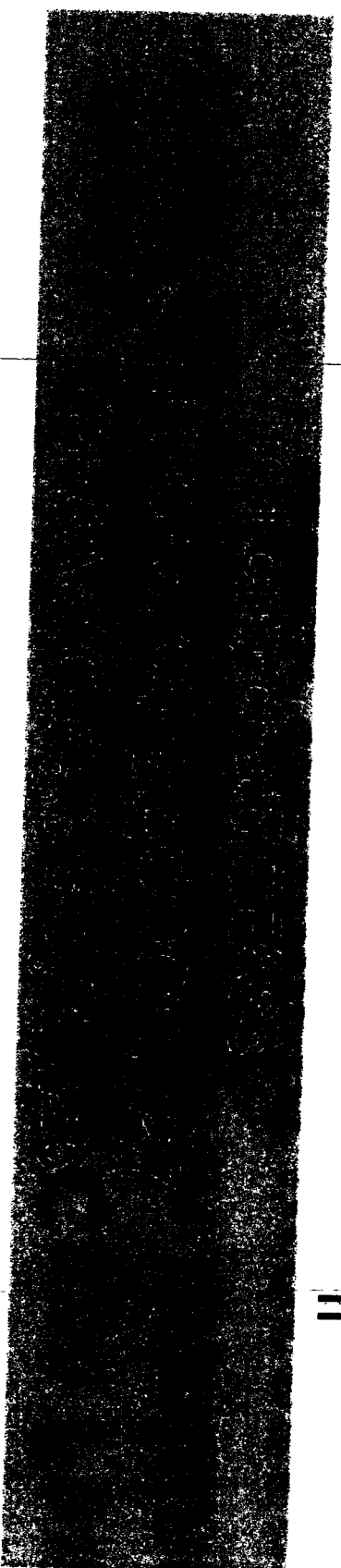
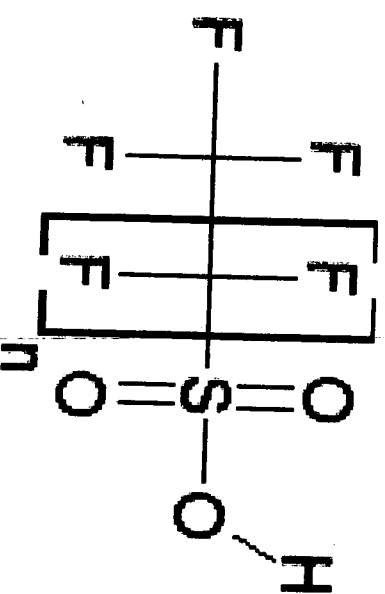
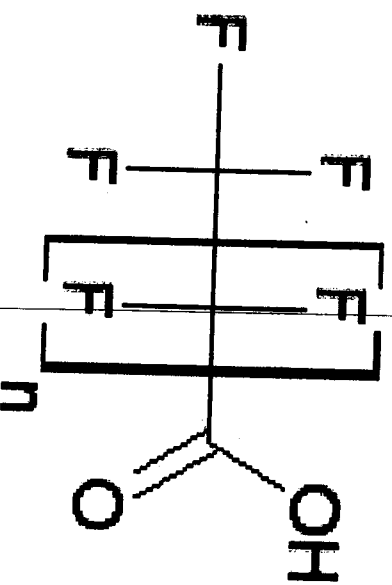
Knappe, D.R.U., Lopez-Velandia, C., Hopkins, Z., and Sun, M. Occurrence of 1,4-dioxane in the Cape Fear River watershed and effectiveness of water treatment options for 1,4-dioxane control. WRRRI Final Report, 2017 (under review).

Sun, M., Arevalo, E., Strynar, M.J., Lindstrom, A.B., Richardson, M., Kearns, B., Smith, C., Pickett, A., and Knappe, D.R.U. "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina." *Environmental Science and Technology Letters*, 3(12): 415-419, 2016a.

Sun, M., Lopez-Velandia, C., and Knappe, D.R.U. "Determination of 1,4-dioxane in the Cape Fear River watershed by heated purge-and-trap preconcentration and gas chromatography-mass spectrometry." *Environmental Science and Technology*, 50(5): 2246-2254, 2016b.

Washington, J.W., Yoo, H., Ellington, J.J., Jenkins, T.M., and Libelo, E.L. "Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA." *Environmental Science and Technology*, 44(22): 8390-8396, 2010.

Perfluoroalkyl acids are organic compounds in which all C-H bonds are replaced with C-F bonds.



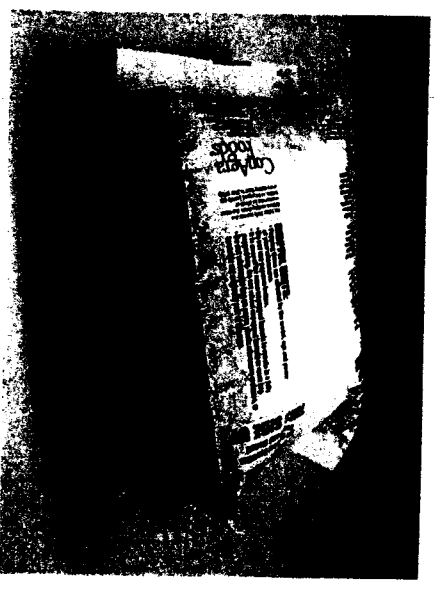
Perfluoroalkyl ether carboxylic acids: Occurrence in the Cape Fear river watershed and fate in drinking water treatment processes

**Mei Sun, Elisa Arevalo, Leigh-Ann Dudley,
Andrew Lindstrom, Mark Strynar, Detlef Knappe**



Long-chain PFASs have long half-lives in humans

- Half-lives in humans
 - PFOA: 3.8 years
 - PFOS: 5.4 years
 - PFBS: 4 months
- Toxicokinetic differences for PFOA
 - 17-19 days in mice
 - 4 hours in female rats



To protect the public from adverse health effects, health based guidelines have been established

EPA Health Advisory (chronic exposure) → PFOS + C8: 70 ng/L

New Jersey guidance level (C8) and recommended MCL (C9) → C8: 40 ng/L
C9: 13 ng/L

Are PFASs a concern in US drinking water?

Six PFASs were included in the third Unregulated Contaminant Monitoring Rule (UCMR3)

Compound	MRL (ng/L)
Perfluoroheptanoic acid (PFHpA, C7)	10
Perfluorooctanoic acid (PFOA, C8)	20
Perfluorononanoic acid (PFNA, C9)	20
Perfluorobutanesulfonic acid (PFBS)	90
Perfluorohexanesulfonic acid (PFHxS)	30
Perfluorooctanesulfonic acid (PFOS)	40



Samples collected from January 2013 – December 2015
Public Water Systems (PWSs) serving >10,000 people

At first glance, UCMR3 data suggest low PFAS detection frequency

UCMR3 requires monitoring for six PFASs in US drinking water.

Monitoring began in 2013, and latest data release was January 2017.

PFAS	MRL (ng/L)	Occurrence (%)	Max. Concentration (ng/L)	Locations with high concentrations
C7	10	0.64	410	Saipan, PA, NY, DE, CO
C8	20	1.03	349	PA, MN, Saipan, DE, WV
C9	20	0.05	56	NJ, DE, PA, MA, NY
PFBS	90	0.05	370	GA, Saipan, CO, AL, PA
PFHxS	30	0.56	1,600	Saipan, AZ, DE, CO, PA
PFOs	40	0.79	7,000	Saipan, DE, CO, PA, WA

36,972 samples from 4,920 PWSs

PFAS detects: 599 samples (1.6%) from 198 PWSs (4.0%)

Of samples with PFAS detects: 23.4% derived from surface water

Some drinking water samples had PFOA+PFOs levels well above the HAL

UCMR3 Data for North Carolina: PFAS detection frequency higher than for entire US

Compound	MRL (ng/L)	NC Detects
Perfluoroheptanoic acid (PFHpA, C7)	10	29 (max. 60 ng/L)
Perfluorooctanoic acid (PFOA, C8)	20	10 (max. 30 ng/L)
Perfluorononanoic acid (PFNA, C9)	20	0
Perfluorobutanesulfonic acid (PFBS)	90	0
Perfluorohexanesulfonic acid (PFHxS)	30	5 (max. 110 ng/L)
Perfluorooctanesulfonic acid (PFOS)	40	8 (max. 90 ng/L)

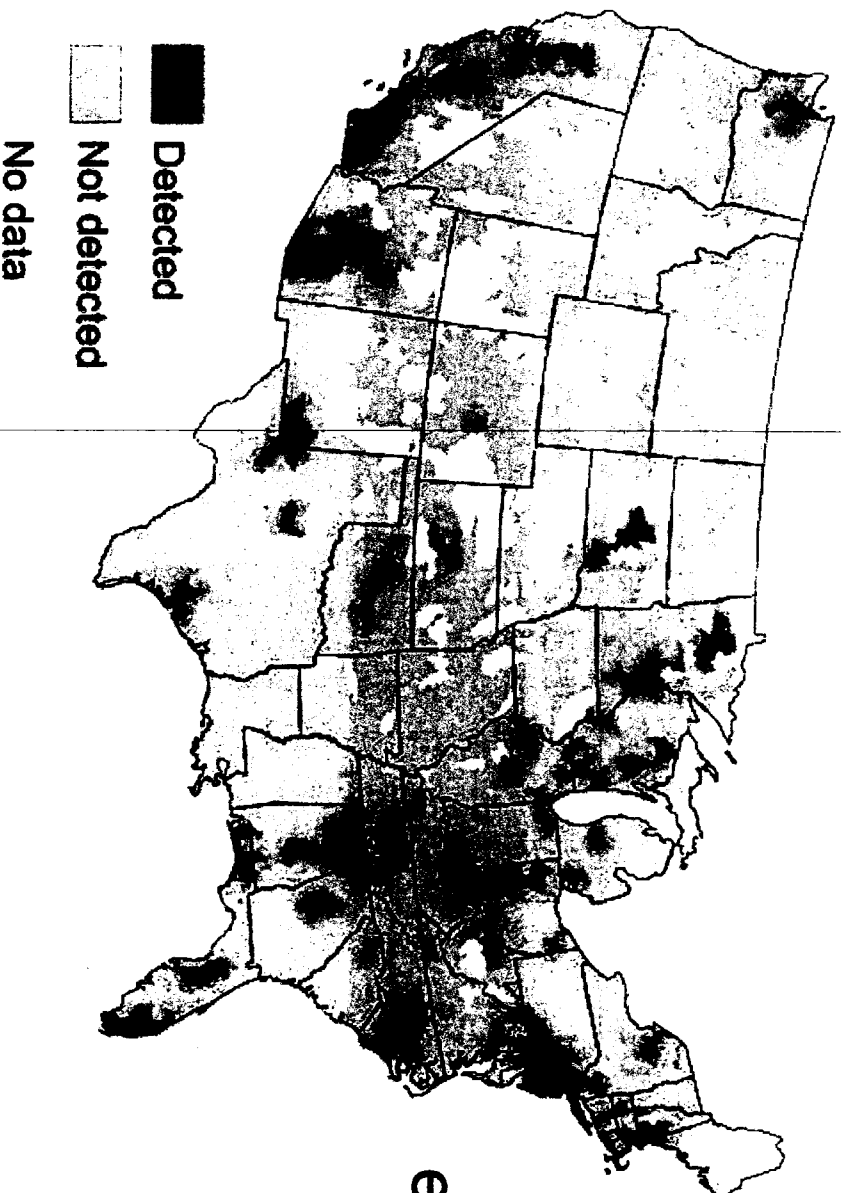
1,320 samples from 151 PWSs in NC

PFAS detects: 43 samples (3.3%) from 20 PWSs (13.2%)

Of samples with PFAS detects: 79% derived from surface water

Elevated PFAS levels affect a sizeable number of US residents

Hydrological units with detectable PFASs



PFOS+PFOA levels estimated to exceed the 70 ng/L HAL in the drinking water of 6 million US residents

Hu et al. ES&T Letters (2016)

**...but are we
seeing the
complete picture?**

Many PFASs are used in commerce

Sub-classes of PFASs

Examples of individual compounds*

Number of peer-reviewed articles since 2002**

PFECAS:
($C_nF_{2n+1}-COOH$)

o PFBA (n=4)	928
o PFPeA (n=5)	698
o PFHxA (n=6)	1081
o PtHPA (n=7)	1186
o PFOA (n=8)	4066
o PFNA (n=9)	1496
o PFDA (n=10)	1407
o PFUnA (n=11)	1069
o PTDAA (n=12)	1016
o PTFrA (n=13)	426
o PTFdA (n=14)	587

PFASs:
($C_nF_{2n+1}-SO_3H$)

perfluoroalkyl acids
(PFAAs)

PFPAAs:
($C_nF_{2n+1}-PO_3H_2$)

PFPIAs:
($C_nF_{2n+1}-PO_2H-C_mF_{2m+1}$)

o PFBS (n=4)	654
o PFHxS (n=6)	1081
o PFOS (n=8)	3507
o PFDS (n=10)	340
o PFBA (n=4)	3
o PFHxPA (n=6)	33
o PFOPA (n=8)	31
o PFDPA (n=10)	35
o C4/C4 PFPA (n,m=4)	4
o C6/C6 PFPA (n,m=6)	12
o C8/C8 PFPA (n,m=8)	12
o C6/C8 PFPA (n=6,m=8)	8

PFECAs & PFESAs:
($C_nF_{2n+1}-O-C_mF_{2m+1}-R$)

o ADONA ($C_3-O-C_3F_6-O-C_6H_4-COOH$)	4
o GenX ($C_3F_7-CF(CF_3)-COOH$)	26
o EEA ($C_2F_5-O-CF_2-O-CF_2-COOH$)	6
o F-538 ($Cl-C_6F_4-O-C_6F_4-SO_3H$)	14

PFASs:
($C_nF_{2n+1}-R$)

PASf-based substances:
($C_nF_{2n+1}-SO_2-R$)

o MeFBSA (n=4, R=N(CH ₃) ₂ H)	25
o MeIOSA (n=8, R=N(CH ₃) ₂ H)	134
o FTFBSA (n=4, R=N(C ₂ H ₅) ₂ H)	7
o FTFOSA (n=8, R=N(C ₂ H ₅) ₂ H)	259
o MeFBSE (n=4, R=N(CH ₃) ₂ C ₄ H ₉ OH)	24
o MeFOSE (n=8, R=N(CH ₃) ₂ C ₄ H ₉ OH)	116
o EtFBSE (n=4, R=N(C ₂ H ₅) ₂ C ₄ H ₉ OH)	4
o EtFOSE (n=8, R=N(C ₂ H ₅) ₂ C ₄ H ₉ OH)	146
o SamBP ([C ₂ F ₅ SO ₂ N(C ₂ H ₅) ₂] ₂ O) ₂ -PO ₃ H ₂)	8
o 100s of others	

PFAA precursors

fluorotelomer-based substances:
($C_nF_{2n+1}-C_2H_4-R$)

o 4,2 FTOH (n=4, R=OH)	106
o 6,2 FTOH (n=6, R=OH)	375
o 8,2 FTOH (n=8, R=OH)	412
o 10,2 FTOH (n=10, R=OH)	165
o 12,2 FTOH (n=12, R=OH)	42
o 6,2 diPAP ([C ₆ F ₁₃ C ₂ H ₅ O] ₂ -PO ₃ H ₂)	23
o 8,2 diPAP ([C ₈ F ₁₇ C ₂ H ₅ O] ₂ -PO ₃ H ₂)	25
o 100s of others	

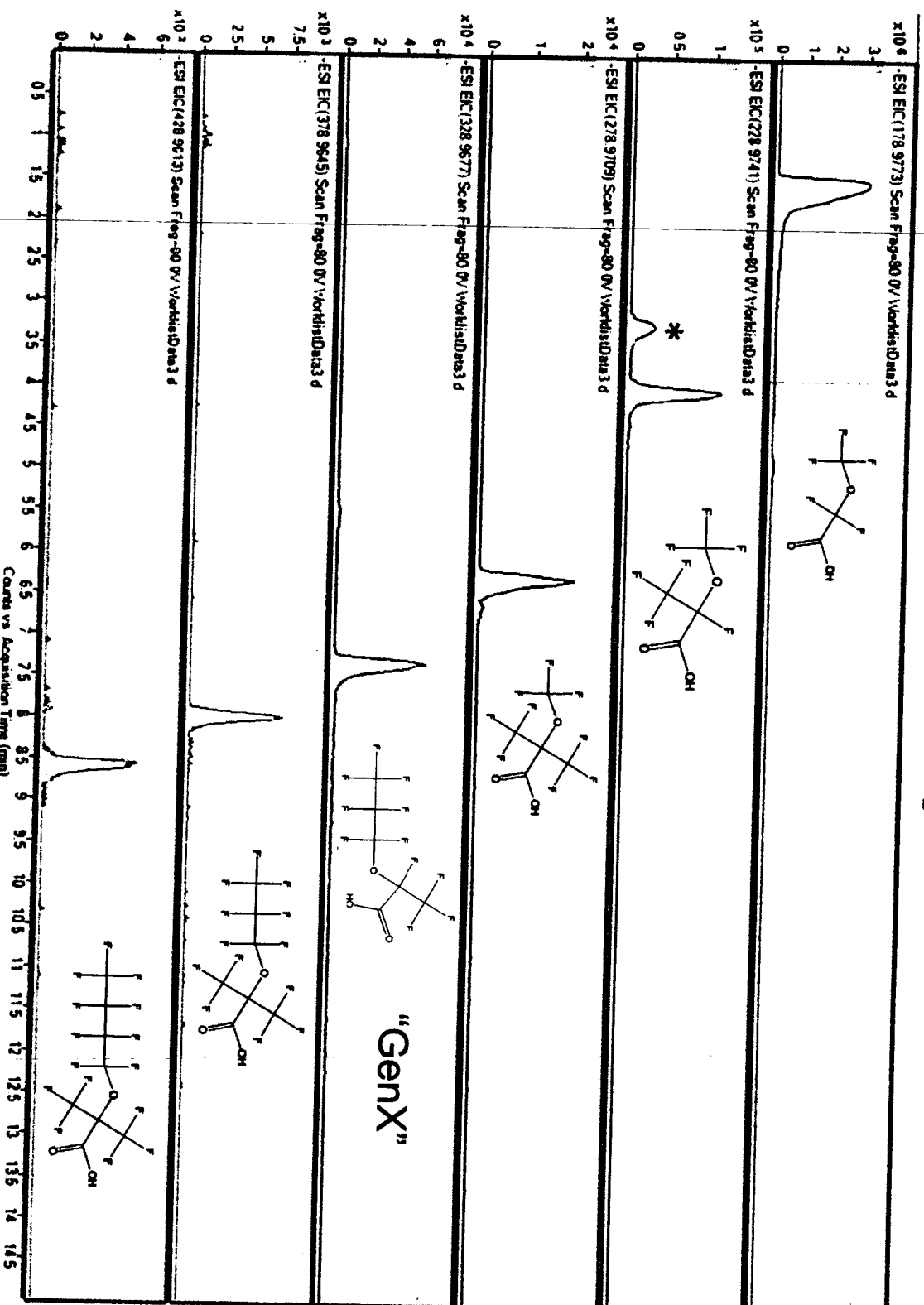
fluoropolymers:

- o polytetrafluoroethylene (PTFE)
- o polyvinylidene fluoride (PVDF)
- o fluorinated ethylene propylene (FEP)
- o perfluoroalkoxy polymer (PFA)

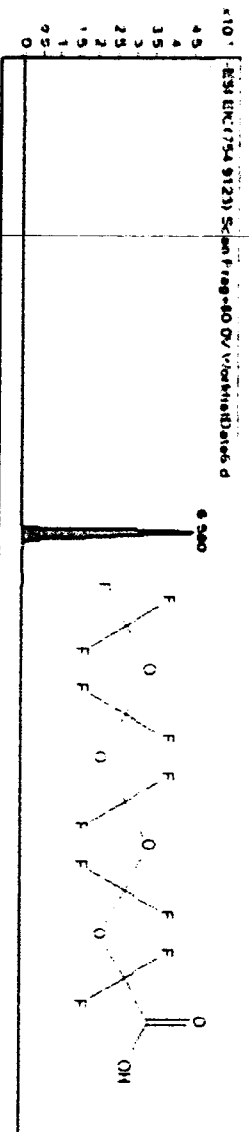
Wang et al. ES&T (2017)

perfluoropolyethers (PFPEs)

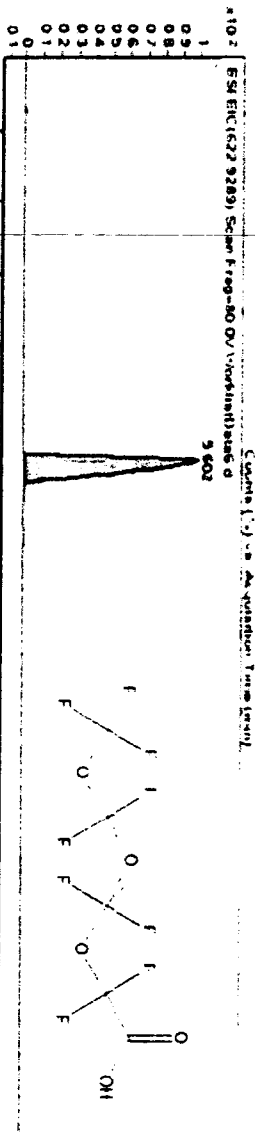
Two series of PFECAs were recently discovered in the Cape Fear River



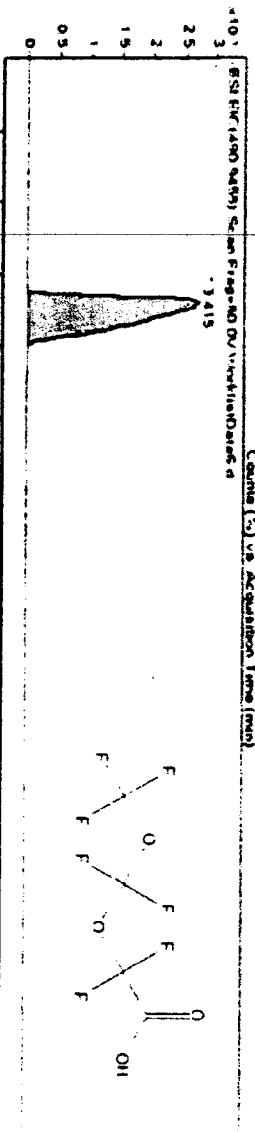
Two series of PFECAs were recently discovered in the Cape Fear River



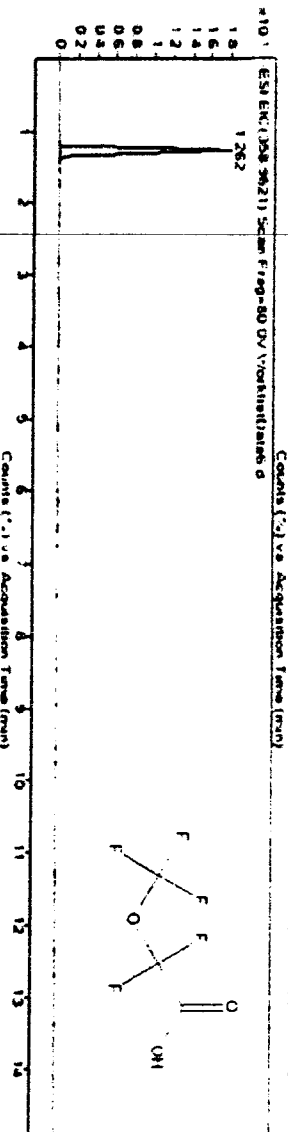
Molecular Formula: $C_{11}H_7F_{11}O_4$
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 [M-H]: 376.9525 Da



Molecular Formula: $C_9H_5F_9O_5$
 Monoisotopic Mass: 311.9880 Da
 [M-H]: 310.9808 Da



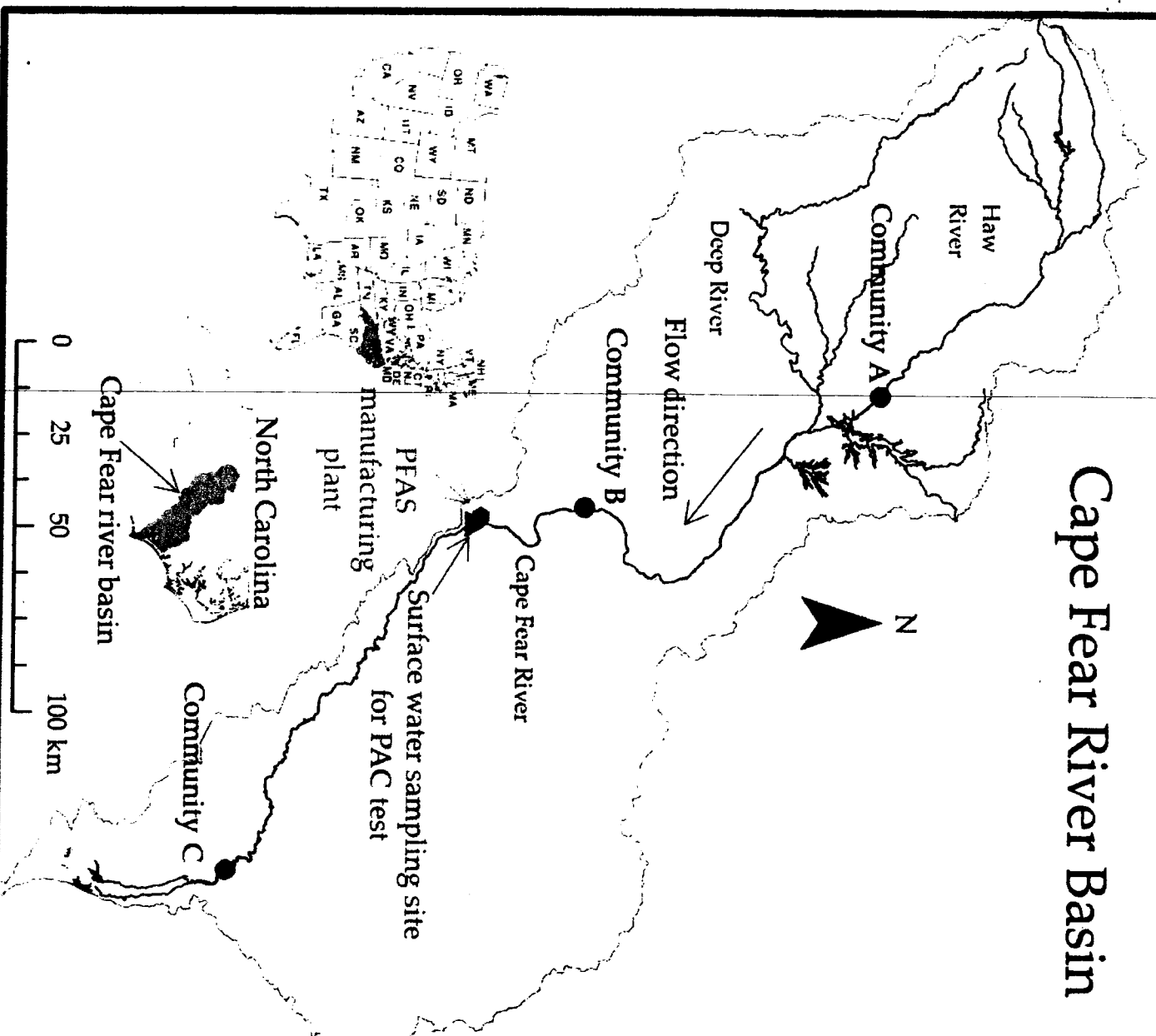
Molecular Formula: $C_{11}H_7F_{10}O_4$
 Monoisotopic Mass: 245.9763 Da
 [M-H]: 244.9690 Da



Molecular Formula: $C_9H_5F_9O_4$
 Monoisotopic Mass: 179.9846 Da
 [M-H]: 178.9773 Da

Study Design

Cape Fear River Basin



- Largest watershed in NC
- Supplies ~1.5M people with drinking water

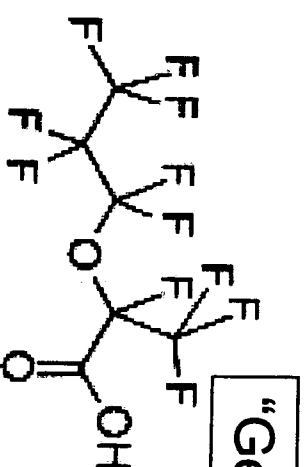
Sampling Protocol

- Samples collected in 1-L HDPE bottles
- Two sampling approaches
 - Daily composite samples of source water at three drinking water treatment plants
 - Grab samples to track PFAS fate in drinking water treatment plant
- No preservative
- Storage at room temperature
- Analysis within 7 days of sample collection

PFAS Analytical Method

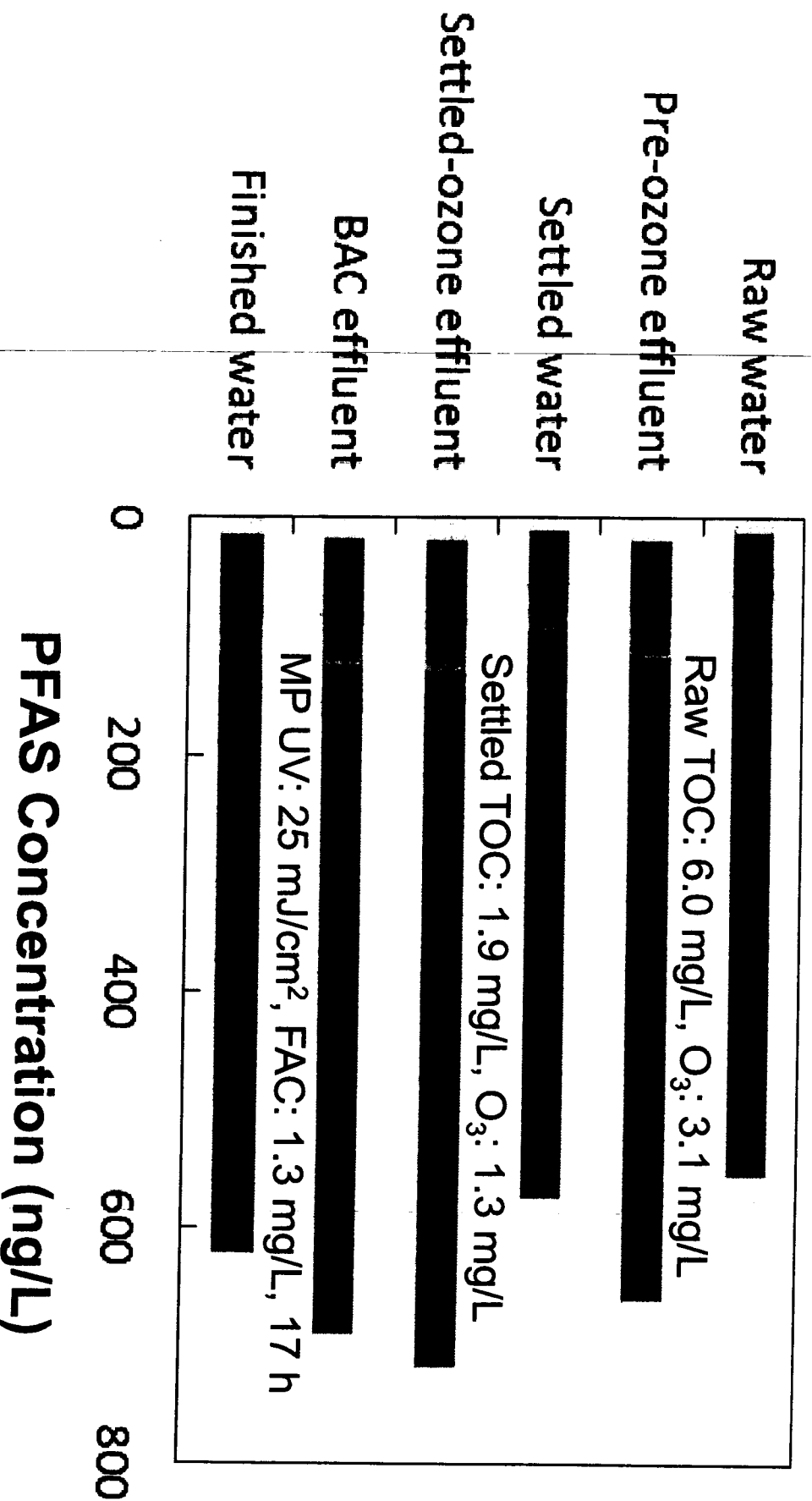
- PFAS concentrations measured by LC-MS/MS
- Large-volume direct injection (900 μ L)
- Sample and standard preparation:
 - filtration with a 0.45- μ m glass fiber filter
 - addition of mass-labeled internal standards
 - addition of formic acid
- Calibration curves ranged from 10 - 750 ng/L
- Limit of quantitation was 10 ng/L for all PFASs except C10 and PFOS (25 ng/L)

PFBA	PFPeA	PFHxA	PFHpA
PFOA	PFNA	PFDA	PFBS
PFHxS	PFOS	PFPrOPrA = "GenX"	



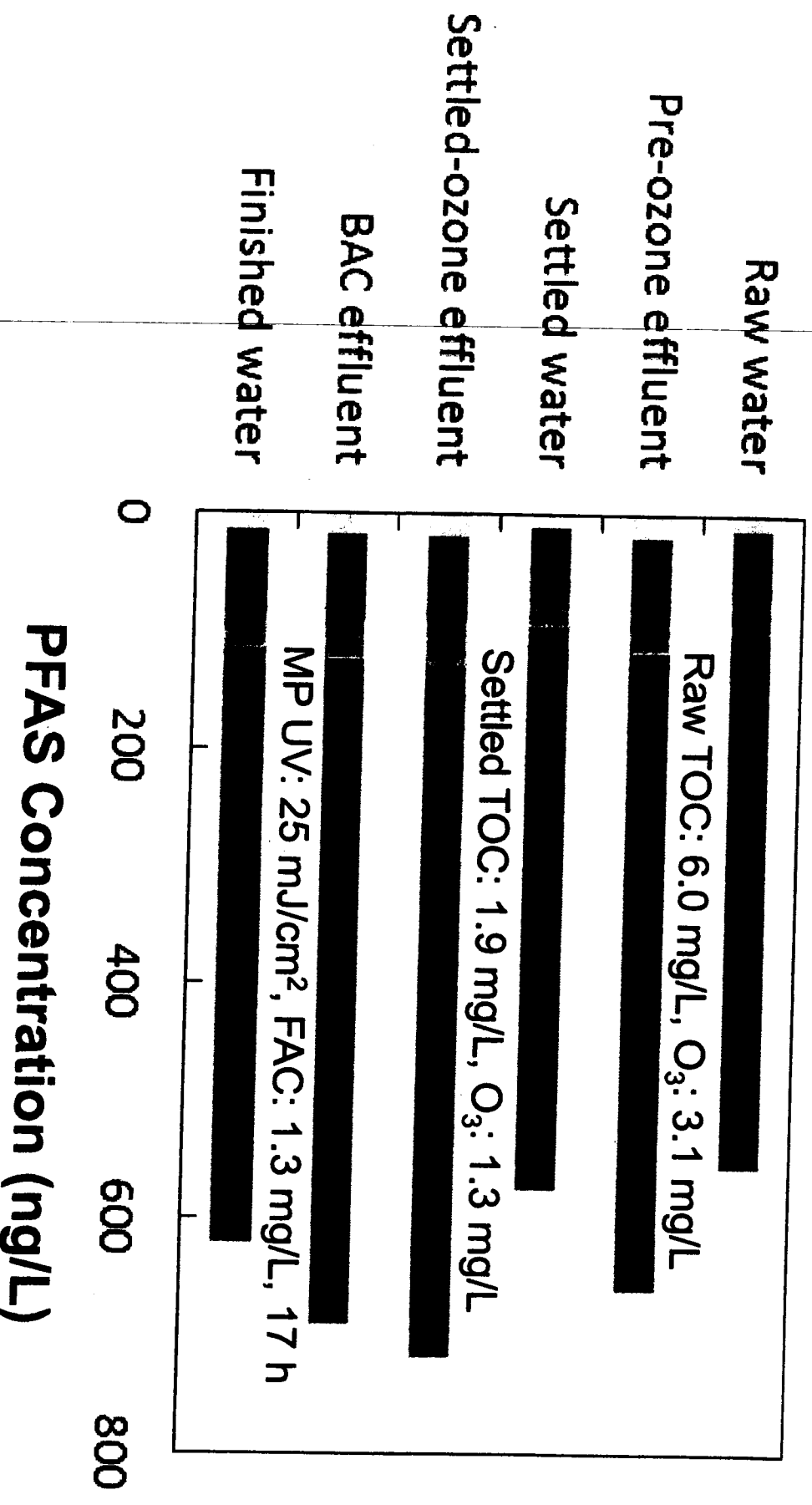
Sun et al. (2016) ES&T Letters

No measurable PFAS removal by conventional and advanced treatment



C4 ■ C5 ■ C6 ■ C7 ■ C8 ■ C9 ■ C10 ■ PFBS ■ PFHS ■ PFOS ■ GenX

No measurable PFAS removal by conventional and advanced treatment



C4 ■ C5 ■ C6 ■ C7 ■ C8 ■ C9 ■ C10 ■ PFBS ■ PFHS ■ PFOS ■ GenX

Condition	Control (%)	MCI (%)	AD (%)
A	100	100	65
B	100	85	55
C	95	90	50
D	85	80	45

■ PFHPA

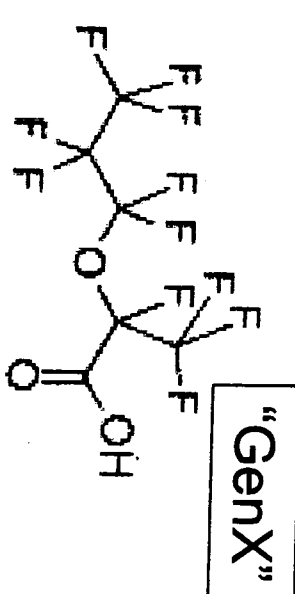
■ **PFBs**

■ PFP_{PRO}RA = “GenX”

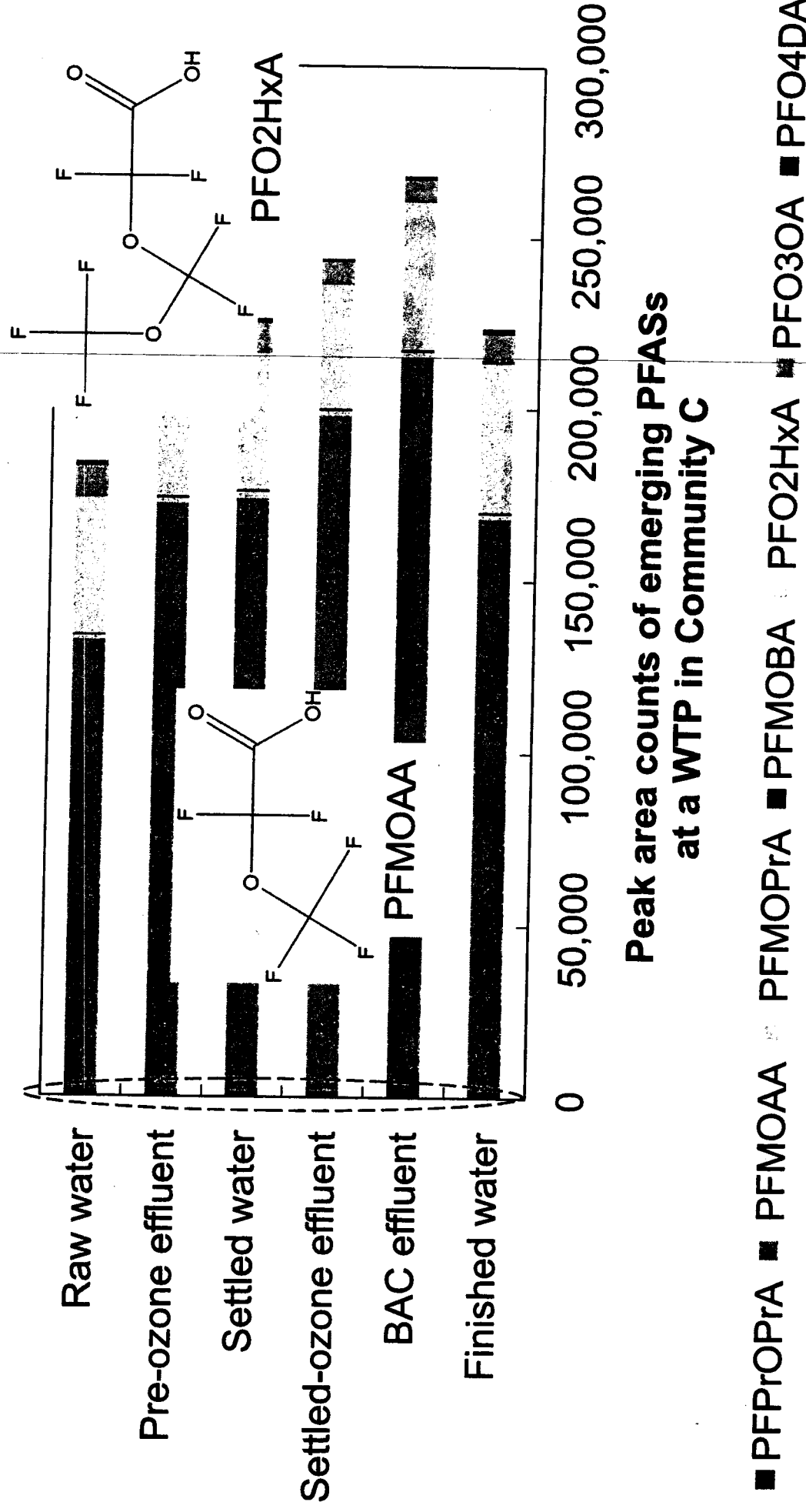
n=127

n=76

$n=35$



Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX



What about activated carbon?

PAC: thermally activated, wood-based

PAC Doses: 30, 60, 100 mg/L

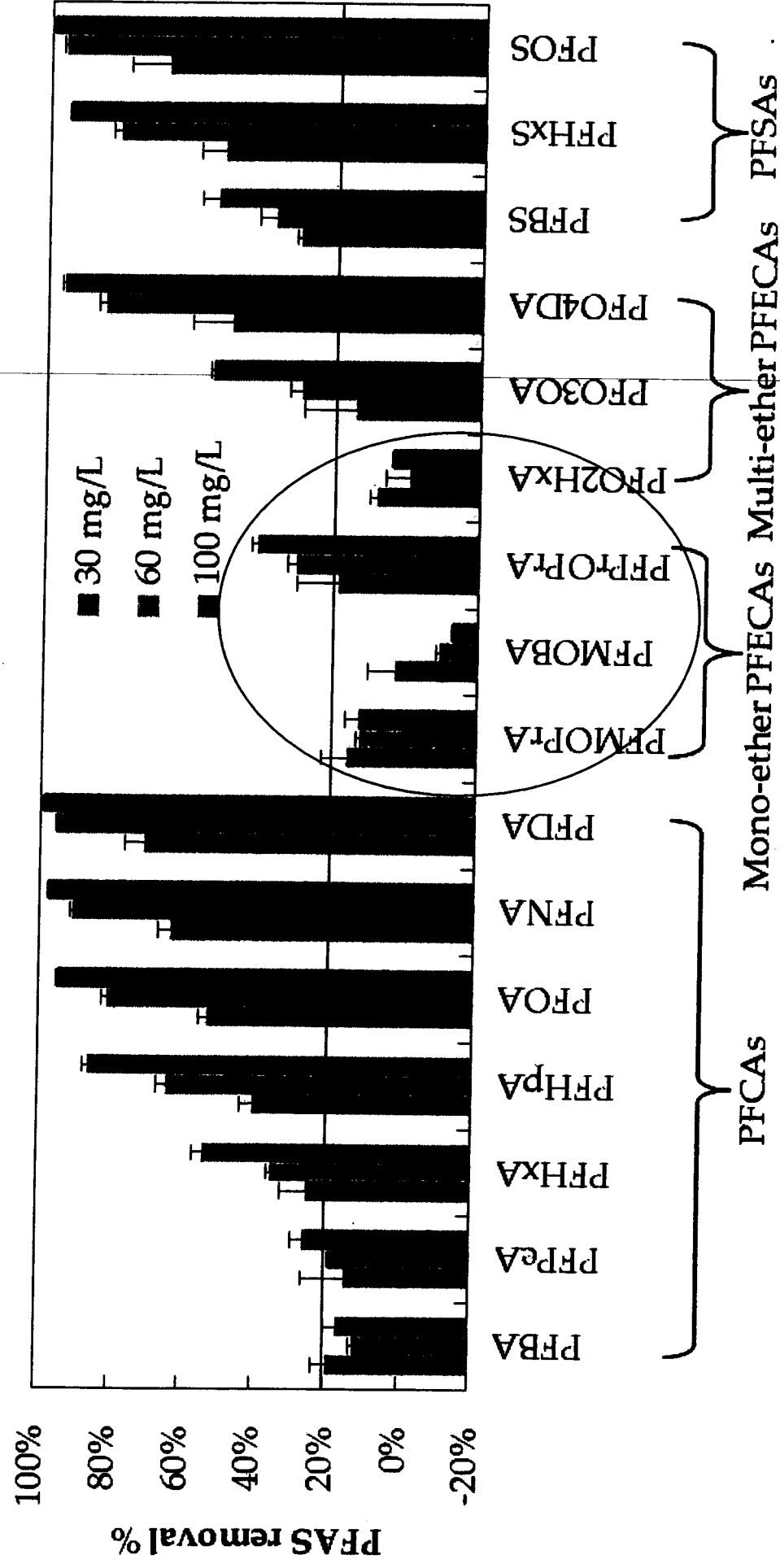
Contact time: 60 minutes

Water: Cape Fear River (TOC: 9.0 mg/L)

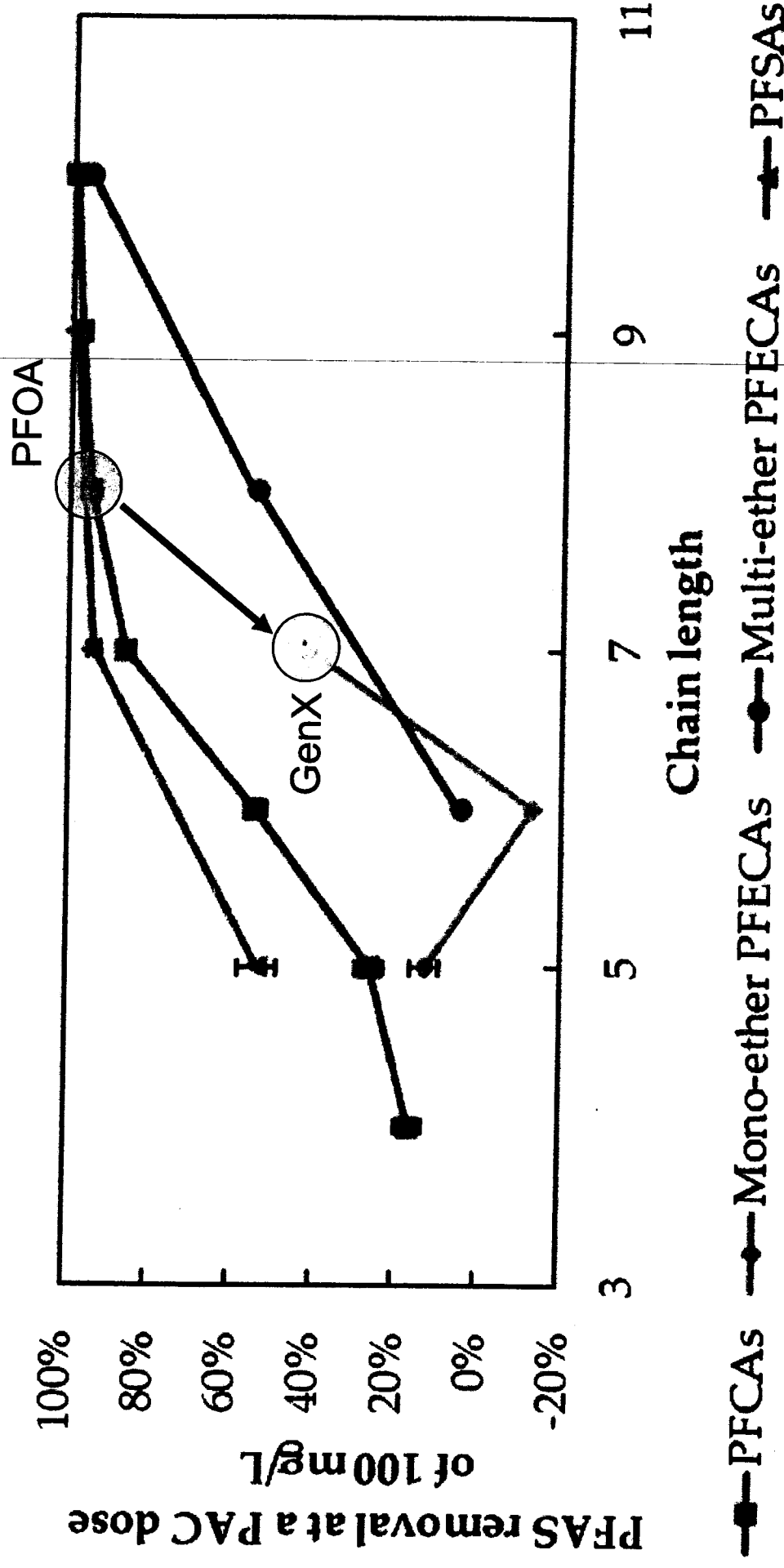
PFECAs: Native levels

PFCAAs and PFSAAs: Spiked at 1000 ng/L

Adsorbability of PFASs varies greatly. The PFECAs that were present at the highest concentrations were essentially non-adsorbable



PFAS adsorbability: PFSA>PFCA>PFECA

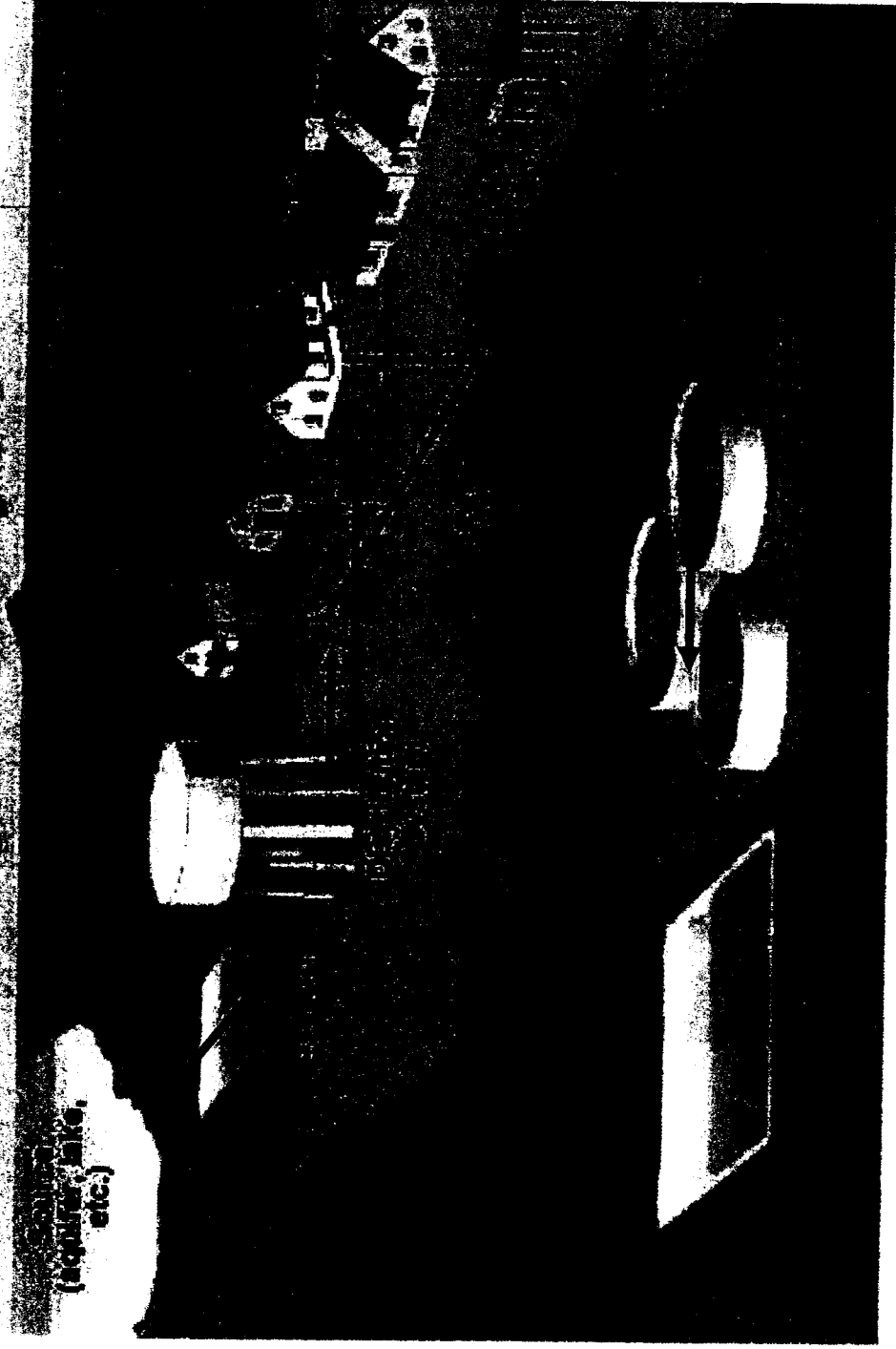


Proposed sampling plan

**1,4-Dioxane and PFAS Fate in
Urban Water Cycle**

Objective 1: Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle

The Drinking Water Cycle



Identify residence times/water ages at suitable sampling points to trace a parcel of water through the water/wastewater system

Objective 2: Determine fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR)

Sample monthly for one ASR cycle (ASR and monitoring wells)

- Recharge
- Storage
- Recovery

Laboratory	Biweekly	Monthly
Cape Fear Public Utilities Authority	Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge)	Total organic carbon, trihalomethanes
NCSU	Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride	1,4-dioxane, PFASs, dissolved organic carbon, UV ₂₅₄ absorbance

Objective 3: Determine possible association of 1,4-dioxane and PFASs with biosolids

Measure 1,4-dioxane and PFAS concentrations in aqueous and solid phases of biosolids. Determine partition coefficients.

Target Audiences for Results

- CFPUA staff
 - Data expected to illustrate treatment/ operational challenges associated with PFASs and 1,4-dioxane
 - Demonstrate need for source control – eliminate PFASs and 1,4-dioxane at upstream NPDES discharge locations
- North Carolina DEQ
 - Raise awareness about treatment challenges with emerging contaminants
 - Expand scope of current 1,4-dioxane working group to start looking at possibilities for controlling PFAS sources

Acknowledgments

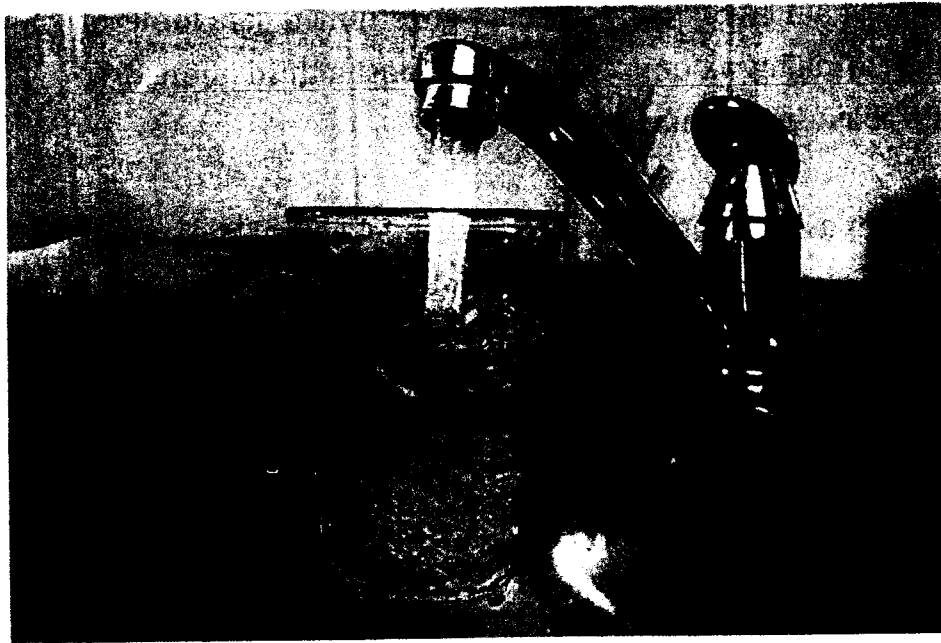
- National Science Foundation (Award #1550222)
- North Carolina Urban Water Consortium
- Adam Pickett, Chris Smith, Michael Richardson, Ben Kearns at participating utilities



HARVARD T.H. CHAN
SCHOOL OF PUBLIC HEALTH

News

Unsafe levels of toxic chemicals found in drinking water for six million Americans



Drinking water samples near industrial sites, military fire training areas, wastewater treatment plants have highest levels of fluorinated compounds

For immediate release: August 9, 2016

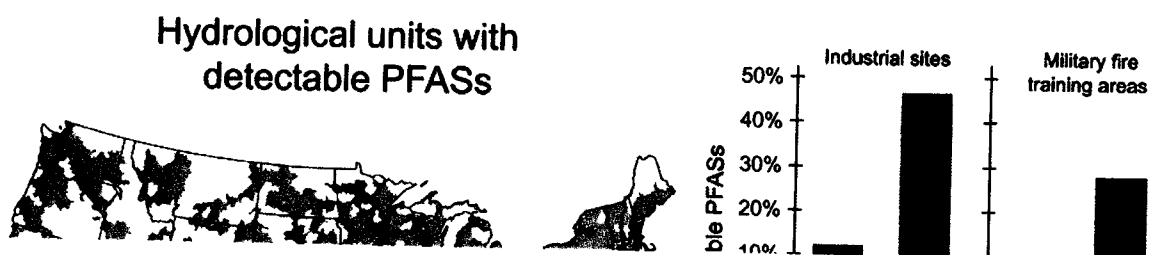
Boston, MA – Levels of a widely used class of industrial chemicals linked with cancer and other health problems—polyfluoroalkyl and perfluoroalkyl substances (PFASs)—exceed federally recommended safety levels in public drinking water supplies for six million people in the U.S., according to a new study led by researchers from Harvard T.H. Chan School of Public Health and the Harvard John A. Paulson School of Engineering and Applied Sciences (SEAS).

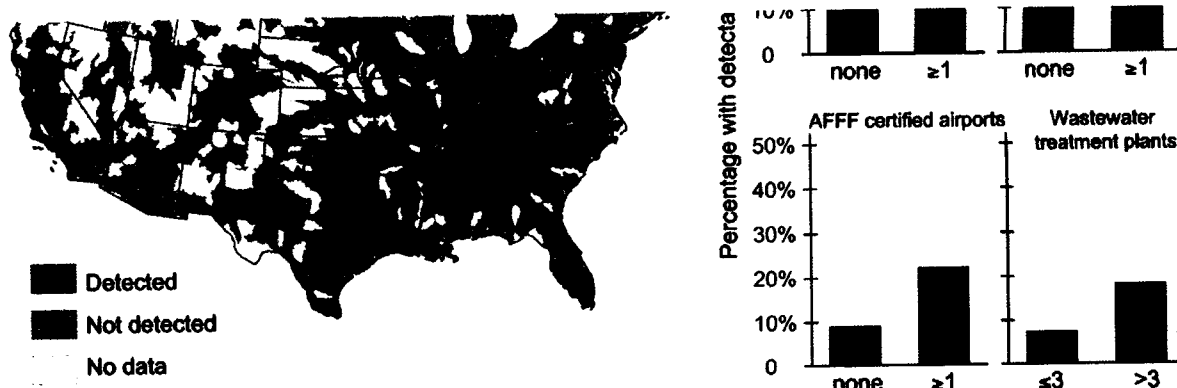
The study will be published August 9, 2016 in *Environmental Science & Technology Letters*.

“For many years, chemicals with unknown toxicities, such as PFASs, were allowed to be used and released to the environment, and we now have to face the severe consequences,” said lead author Xindi Hu, a doctoral student in the Department of Environmental Health at Harvard Chan School and Environmental Science and Engineering at SEAS. “In addition, the actual number of people exposed may be even higher than our study found, because government data for levels of these compounds in drinking water is lacking for almost a third of the U.S. population—about 100 million people.”

PFASs have been used over the past 60 years in industrial and commercial products ranging from food wrappers to clothing to pots and pans. They have been linked with cancer, hormone disruption, high cholesterol, and obesity. Although several major manufacturers have discontinued the use of some PFASs, the chemicals continue to persist in people and wildlife. Drinking water is one of the main routes through which people can be exposed.

The researchers looked at concentrations of six types of PFASs in drinking water supplies, using data from more than 36,000 water samples collected nationwide by the U.S. Environmental Protection Agency (EPA) from 2013–2015. They also looked at industrial sites that manufacture or use PFASs; at military fire training sites and civilian airports where fire-fighting foam containing PFASs is used; and at wastewater treatment plants. Discharges from these plants—which are unable to remove PFASs from wastewater by standard treatment methods—could contaminate groundwater. So could the sludge that the plants generate and which is frequently used as fertilizer.





This map is based on publicly available data provided by the U.S. EPA (<https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule>). Areas highlighted in blue indicate zip codes where PFASs were detected in one or more water samples from 2013–15 that were at or above the minimum reporting levels required by the U.S. EPA. Zip codes that are elevated in PFASs do not represent all drinking water sources in that region. Individuals concerned about their drinking water should consult with their local water suppliers. More detailed maps based on the U.S. EPA data are available from the Environmental Working Group (<http://www.ewg.org/enviroblog/2015/08/your-drinking-water-contaminated-toxic-non-stick-chemicals>).

Credit: Hu et al, *Environmental Science & Technology Letters*
<http://pubs.acs.org/doi/pdf/10.1021/acs.estlett.6b00260>

The study found that PFASs were detectable at the minimum reporting levels required by the EPA in 194 out of 4,864 water supplies in 33 states across the U.S. Drinking water from 13 states accounted for 75% of the detections, including, in order of frequency of detection, California, New Jersey, North Carolina, Alabama, Florida, Pennsylvania, Ohio, New York, Georgia, Minnesota, Arizona, Massachusetts, and Illinois.

Sixty-six of the public water supplies examined, serving six million people, had at least one water sample that measured at or above the EPA safety limit of 70 parts per trillion (ng/L) for two types of PFASs, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). Concentrations in some locations ranged as high as 349 ng/L for PFOA and 1,800 ng/L for PFOS.

The highest levels of PFASs were detected in watersheds near industrial sites, military bases, and wastewater treatment plants—all places where these chemicals may be used or found.

“These compounds are potent immunotoxicants in children and recent work suggests drinking water safety levels should be much lower than the provisional guidelines established by EPA,” said Elsie Sunderland, senior author of the study and associate professor in both the Harvard Chan School and SEAS.

Other Harvard Chan authors of the study included Philippe Grandjean and Courtney Carignan.

Funding for the study came from the Smith Family Foundation and a private donor.

“Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants,” Xindi C. Hu, David Q. Andrews, Andrew B. Lindstrom, Thomas A. Bruton, Laurel A. Schaider, Philippe Grandjean, Rainer Lohmann, Courtney C. Carignan, Arlene Blum, Simona A. Balan, Christopher P. Higgins, and Elsie M. Sunderland, *Environmental Science & Technology Letters*, online August 9, 2016, doi: 10.1021/acs.estlett.6b00260

Note: This release was updated on August 10 and August 11, 2016.

From the authors of the Environmental Science & Technology Letters study: We have mapped watersheds in the United States that have potentially high concentrations of PFASs based on U.S. EPA data. This does not mean that all drinking water supplies within the highlighted regions contain high PFAS concentrations, but that at least one sample from at least one water supply was reported to be at or above levels considered safe by the U.S. EPA between 2013 and 2015. However, no measurements have been made in many water supplies across the country. We recommend increased monitoring of these contaminants in our drinking water. For more information, please contact the U.S. EPA: Cathy Milbourn, Milbourn.cathy@Epa.gov, 202-564-7849 or Monica Lee, Lee.monica@Epa.gov, 202-564-0645.

PFASs and reduced immune response

Another Harvard Chan School study, led by Grandjean, adjunct professor of environmental health, published in *Environmental Health Perspectives*, also suggested negative health impacts of PFAS exposure. That study looked at a group of about 600 adolescents from the Faroe Islands, an island country off the coast of Denmark. Those exposed to PFASs at a young age had lower-than-expected levels of antibodies against diphtheria and tetanus, for which they had been immunized. The findings suggested that PFASs, which are known to interfere with immune function, may be involved in reducing the effectiveness of vaccines in children.

Funding for this study came from the National Institute of Environmental Health Sciences, NIH (ES012199); the U.S. Environmental Protection Agency (R830758); the Danish Council for Strategic Research (09-063094); and the as part of the environmental support program DANCEA (Danish Cooperation for Environment in the Arctic).

“Serum Vaccine Antibody Concentrations in Adolescents Exposed to Perfluorinated Compounds,” Philippe Grandjean, Carsten Heilmann, Pal Weihe, Flemming Nielsen, Ulla B. Mogensen, and Esben Budtz-Jørgensen, *Environmental Health Perspectives*, online August 9, 2016, doi: 10.1289/EHP275

Visit the Harvard Chan School website for the latest news, press releases, and multimedia offerings.

For more information:

Marge Dwyer
617.432.8416
mhdwyer@hsph.harvard.edu

photo: iStockphoto.com

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Harvard T.H. Chan School of Public Health brings together dedicated experts from many disciplines to educate new generations of global health leaders and produce powerful ideas that improve the lives and health of people everywhere. As a community of leading scientists, educators, and students, we work together to take innovative ideas from the laboratory to people's lives—not only making scientific breakthroughs, but also working to change individual behaviors, public policies, and health care practices. Each year, more than 400 faculty members at Harvard Chan School teach 1,000-plus full-time students from around the world and train thousands more through online and executive education courses. Founded in 1913 as the Harvard-MIT School of Health Officers, the School is recognized as America's oldest professional training program in public health.

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draft to
exec committee

Dear Ms. Sheila Holman,

The Cape Fear Public Utility Authority provides water and sewer service to nearly 200,000 customers in New Hanover County and the City of Wilmington in southeastern North Carolina. In addition to obtaining raw water from various groundwater sources, the Authority obtains surface water from the Cape Fear River just upstream of Lock & Dam # 1 in Bladen County, for treatment at the Sweeney Water Treatment Plant, and distribution to customers. The Sweeney Water Treatment Plant uses advanced treatment processes such as advanced coagulation/flocculation/sedimentation, ozone and UV, and BAC filtration.

Following a review of recent research we have become aware that since the year 2000, a number of per and poly-fluoroalkyl substances have been introduced onto the market to replace long chain perfluoroalkyl acids (e.g. perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) and their respective precursors. This research indicates these poly-fluoroalkyl substances are present in the Lower Cape Fear River source water. These compounds are currently not regulated at the state or federal levels governing discharges into this river. Due to the persistence of these compounds and the ineffectiveness of existing water treatment technologies in removing these compounds, these substances should be regulated at the point of discharge into the river to prevent downstream long term health concerns.

Please find herewith a publication titled "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminates in the Cape Fear River Watershed of North Carolina" for your reference. As this is newly available information, your assistance in evaluating this situation would be appreciated. Furthermore, we would support actions identified by NCDEQ to ensure proper regulation and management of the dischargers for the protection of the river and its users. If additional information or assistance is needed, please contact me.

Sincerely,

James R. Flechtner, Executive Director

Cape Fear Public Utility Authority

Copy:

Jay Zimmerman, Director NCDWR

Julie Grzyb, NPDES Permitting Supervisor

Jessica Godreau, PWS Section Chief

TO: Cape Fear Public Utility Authority Board of Directors

FROM: Jennifer H. Adams
Robin W. Smith

RE Review of GenX Response

DATE: June 22, 2017

Scope of Report: Review of timeline of the GenX issue; information available to staff of CFPUA; appropriateness of response to the developing information; identification of possible future steps.

I. Timeline of actions related to GenX (attached).



Timeline.doc

II. Background on regulation of GenX. The U.S. Environmental Protection Agency (EPA) began studying the effects of perfluorinated compounds like PFOA and PFOS (used in firefighting foam, water repellants, Teflon, and other products) over fifteen years ago. As concern about health effects and persistence in the environment grew, EPA worked with chemical companies to phase-out the two compounds. In 2000, 3M announced that it would stop production of PFOS. Under a 2006 voluntary agreement with EPA, eight companies committed to phase out PFOA by 2015. As the companies moved to phase-out PFOA and PFOS, they began to develop new compounds like GenX to replace them. Use of new compounds has been phased in within the last 5-10 years.

A. *Safe Drinking Water Act.* Public water systems like Cape Fear Public Utility Authority meet drinking water standards adopted by EPA under the federal Safe Drinking Water Act.

- ◆ EPA has adopted drinking water standards for nearly 90 contaminants; standards do not exist for many compounds used in manufacturing or produced as a by-product of industrial activities. Example: hexavalent chromium
- ◆ EPA has not set drinking water standards for any perfluorinated compounds.

◆ In 2012, EPA required large public water systems to monitor for six unregulated perfluorinated compounds (including PFOA and PFOS) to gather information on the occurrence of those compounds in drinking water and published the results in January 2017. The “unregulated contaminant” monitoring requirement did not cover alternatives like GenX.

◆ Prior to 2016, EPA had a provisional health advisory for PFOA and PFOS (combined) of 600 ng/L based on short-term exposure. On May 25, 2016, EPA issued an updated health advisory for PFOA and PFOS (combined) of 70 parts per trillion (= 70 ng/L) based on life-time exposure. EPA has said the health advisory level does not apply to other PFAS and EPA has not decided whether to adopt a drinking water standard for PFOA and PFOS. That decision would be based on: 1. likelihood the contaminants will be found in drinking water; 2. the health effects of the contaminant; and 3. the technical/economic feasibility of treating the water to reduce any health risk.

B. Clean Water Act Wastewater Discharge Permits

◆ PFAS are not on EPA’s list of priority toxic pollutants

◆ It does not appear that any state has adopted an in-stream water quality standard for PFAS

◆ EPA has set technology-based wastewater limits for individual categories of industries, including chemical plants.

◆ In the absence of an existing EPA limit, the state permit writer can set a limit based on best professional judgment. From the NPDES Permit Writer’s Manual:

“Without applicable effluent guidelines for the discharge or pollutant, permit writers must identify any [limits] on a case-by-case basis, in accordance with the statutory factors specified in CWA sections 301(b)(2) and 304(b).”

III. The 2016 Knappe Paper. In 2015, Cape Fear Public Utility Authority staff agreed to cooperate with Dr. Detlef Knappe of North Carolina State University to look at concentrations of newer fluorinated alternatives (perfluoroalkyl ether carboxylic acids or “PFECAs”) between a known source of fluorochemicals – the Chemours plant in Fayetteville -- and the Sweeney water treatment plant. GenX is a PFECA. The study also looked at the effectiveness of drinking water treatment in removal of those compounds.

For comparison, researchers took raw water samples at two water treatments plants upstream of Chemours– one on the Haw River and the other below Jordan Lake. The research detected older, legacy PFAS (PFOA and PFOS) at the two upstream plants, but very low levels of PFOA/PFOS in raw water at the Sweeney plant. At the Sweeney plant, the sampling detected GenX at an

average concentration of 631 ppt (= 631 ng/L). Six other PFECAs were also detected, but were not quantified.

The Knappe paper noted the lack of published information on the toxicity or environmental fate of PFECAs and the possible need for more work on discharge control and contaminant monitoring. The paper was shared with staff in DEQ's Division of Water Resources and other state and federal agencies.

IV. Findings

CFPUA staff actively participated in the Knappe study to learn more about the possible impact of emerging fluorochemicals on the water supply, as well as their fate in water treatment processes.

The study appears to have been one of the first studies of PFECAs in water supplies. The analytical methods for detecting the compounds were just being developed during the time Dr. Knappe began collecting data in 2013-2014.

The Knappe report provided data on the concentrations of GenX and other PFECAs in the raw water supply, but noted the lack of published information on the toxicity and environmental fate of the contaminants.

EPA has not issued a drinking water standard for PFECAs, so the findings of the Knappe report had no immediate regulatory implications for CFPUA. There was also no health advisory for PFECAs to provide a benchmark for advising the public of any risk.

Discussion of the Knappe report results and next steps resumed in March and April of 2017. CFPUA staff met with Dr. Knappe about a possible follow up study to monitor concentrations of GenX in the water delivery system. CFPUA staff also conferred with NC DEQ about getting the state's assistance to further investigate and regulate the discharge from Chemours.

When the story broke in June of 2017, the CFPUA exec committee was engaged with NC DEQ and requesting assistance in evaluating the effect of GenX on surface water.

V. Conclusion. Given all of the available information, it is our opinion that CFPUA staff acted in an appropriate, professional, timely, and scientific manner. Data was gathered, studied, and reviewed at appropriate levels. Based upon information and facts available to CFPUA at the time, staff moved the issue appropriately through the CFPUA chain of command.

VI. Recommendations

- Consider a process for releasing "non-routine" sampling results to the public.

Sources:

EPA: News release concerning phase-out of PFOS

<https://yosemite.epa.gov/opa/admpress.nsf/0/33aa946e6cb11f35852568e1005246b4>

EPA: Fact sheets on PFOA Stewardship Program <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program>

EPA: NPDES Permitting of Wastewater Discharges from Chemical Plants

<https://www.epa.gov/eg/organic-chemicals-plastics-and-synthetic-fibers-effluent-guidelines>

EPA Permit Writers Manual: **National Pollutant Discharge Elimination System (NPDES) Permit Writers Manual: Chapter 5 - pwm_chapt_05.pdf**

EPA: Priority Toxic Pollutant **Toxic and Priority Pollutants Under the Clean Water Act | Effluent Guidelines | US EPA**

EPA: Drinking Water Standards **Drinking Water Contaminants – Standards and Regulations | US EPA**

EPA: Health Advisories for PFOA and PFOS **Drinking Water Health Advisories for PFOA and PFOS - drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf**

EPA: The 3rd Unregulated Contaminant Rule **The Third Unregulated Contaminant Monitoring Rule (UCMR 3): Data Summary, January 2017 - ucmr3-data-summary-january-2017.pdf**

EPA: Monitoring unregulated contaminants **Monitoring the Occurrence of Unregulated Drinking Water Contaminants | US EPA**

EPA: National Primary Drinking Water Standards **National Primary Drinking Water Regulation Table | Ground Water and Drinking Water | US EPA**

Legacy and Emerging Perfluoroalkyl Substances are Important Drinking Water Contaminants in the Cape Fear River Watershed of N.C., Detlef Knappe and others, Environmental Science and Technology Letters, Publication date (Web) November 10, 2016.

Documents, including email, between CFPUA and Detlef Knappe related to the National Science Foundation grant application to study perfluoroalkyl substances in the Cape Fear River and development of the study.

CFPUA records, including email, of meetings and other communications following publication of the Knappe paper.

CFPUA GenX Timeline Investigation

Rev 1 (6/27/17)

	Genesis of the initial study was the interest of NCSU research group (lead by Dr. Detlef Knappe) & EPA collaborators to learn which compound replaced PFOA, the polymer processing aid Dupont/Chemours had been making at the Fayetteville site. No one requested the study. Knappe's recollection is that EPA colleagues first identified GenX as the PFOA replacement in 2012.
6/14/13-10/13/13	Knappe team obtains an analytical standard for GenX and analyzes multiple samples of Sweeney raw water feed. Knappe does not recall if those sample results were provided to CFPUA at that time.
	At this point in time, EPA had a provisional health advisory level of 600 ng/L (PFOA & PFOS combined).
5/30/14	Knappe (NCSU) to Richardson (CFPUA): request for assessment of Sweeney, Brunswick, & Pender for 1,4-dioxane & perfluorinated compound removal. Quick assessment of wide range of treatment technologies.
7/1/14	Knappe to Hawley (CFPUA): confirming NCSU trip to Sweeney; no confirmation from Brunswick (Glenn Walker) ; Pender expressed interest (Brandon Garner)
8/13/14	Knappe to Hawley: confirmed sampling visit on 8/18 for purposes of collecting a few water samples for 1,4-dioxane & polyfluorinated ether analysis. Samples collection proposed from various unit ops in water treatment process.
8/18/14	Sampling of unit processes through the Sweeney WTP was completed by Knappe's team.
10/13/14	Knappe to Richardson: Knappe writing a proposal to NSF to study the occurrence of fluorochemicals in the CF River and to assess/develop treatment options. Offered co-principal investigator status to Richardson.
6/10/15	Richardson to Knappe: Confirmed study participation and co-PI status; goal to closely collaborate to facilitate knowledge transfer.
8/26/15	Richardson to Flechtner: Knappe NSF proposal sent for approval. Goal of study: "Because of their persistence, bioaccumulation potential and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are being replaced with short-chain PFASs and fluorinated alternatives. Almost no information exists about the occurrence of fluorinated alternatives and their behavior during water treatment. The overall goal of the proposed research is to begin to fill this knowledge gap by studying one class of fluorinated alternatives, perfluoro(poly)ethers (PFPEs). Research objectives include (1) develop a method for analysis... (3) apply the method to Sweeney WTP samples.... Results are expected to provide the basis for a broader investigation of the behavior of fluorinated alternatives in natural and engineered systems."
	Consider this to be a second study to confirm the presence of additional perfluoroalkyl ether carboxylic acids (PFECAs). GenX is only one type of PFECAs, there are 3 others as well.
8/26/15	Knappe to Flechtner, Richardson: email re: collaborative project between NCSU & CFPUA. Goal is to study the fate of perfluorinated ethers in the CFR from the point of discharge near Fayetteville to your drinking water intake. In addition, we are planning to evaluate the treatment effectiveness of individual unit processes at the Sweeney WTP. Mike is a co-PI on the project.
8/27/15	Signed agreement returned to Knappe from Flechtner, "This looks like an interesting and valuable study and I look forward to seeing the findings."
5/3/16	Knappe sends email to Richardson: share beginnings of paper on occurrence of perfluoroalkyl substances in CFR. Contained with abstract "The only PFECA for which an authentic standard was available for quantification, GenX, was detected at an average concentration at 631 ng/L." Richardson forwards email to Kearns (Rev 1).

5/25/16	EPA reduces the health advisory limit for PFOA & PFOS to 70 ng/L.
9/12/16	Richardson & Styers meeting; reviewed Knappe report. "Good thing to be published and get information out there on emerging contaminants."
9/18/16	Knappe to Kearns, Richardson, and 3 other study participants: Will be sending manuscript to Environmental Science & Technology Letters on 9/26/16. Includes occurrence data for perfluorinated compounds. Sent draft research paper; requested final comments before publication submission on 9/26/16.
9/24/16	Knappe to Kearns, Richardson: interest in co-authorship on paper? Response "Yes, grateful if you added us as co-authors. Do not have any comments on it at this time". Added as co-authors since they provided samples.
9/30/16	Richardson retires from CFPUA
11/10/16	Knappe paper published in Environmental Science & Technology Letters, "Legacy & Emerging Perfluoroalkyl Substances are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina". Co-authors include CFPUA, US EPA, Town of Pittsboro, and Fayetteville Public Works Commission. Study found that for PFAS compounds, which the EPA had already established health advisories for, were not found at high levels in the CFR. The paper also indicated that there was little information on the toxicity of the fluorochemical alternatives (PFECAs) found in the CFR, and that EPA has not established a health advisory standard for those PFECAs.
11/19/16	<i>Knappe sends paper to co-authors, including Kearns & Richardson. (Rev 1)</i>
11/23/16	Knappe forwards published paper to multiple individuals within NC DEQ and various cities (CFPUA not included in email). Text of email includes "attaching a paper we published this month in ES&T Letters. We studied the occurrence of per- and polyfluoroalkyl substances (PFAS) in the Cape Fear River watershed. Legacy PFAS, such as PFOA and PFOS dominated the PFAS signature in the Haw River, In contrast, new fluorinated alternatives such as GenX, a replacement for PFOA, were very high in Wilm (and by association also in Brunswick and Pender). None of the newly discovered compounds being discharged by the Chemours plant south of Fayetteville are removed by the advanced and conventional treatment processes employed in the Sweeney WTP in Wilm. Also, many of the compounds are essentially non-adsorbable on activated carbon. I think it would be useful to discuss the results. A large number of people are exposed to high levels of PFAS through their drinking water!"
11/29/16	Dr. Mallin (UNCW) sends email stating "Folks – recent CFR paper from NCSU", with attached published paper. Recipients include personnel from UNCW, NC DENR, NOAA, NCSU, Fayetteville Public Works, CFPUA (Eckert & Ellis), Cape Fear River Watch & NC Coastal Federation
3/6/17	Knappe sends published paper to Kearns
3/7/17	Kearns forwards paper to Eckert, Deane, & Allyson Ridout (all CFPUA internal).
3/7/17	Kearns to Deane: would be good to investigate whether a lab can analyze for emerging compounds highlighted in study.
3/20/17	Styers, Eckert, Vandermeiden, and Flechtner meet to discuss Knappe paper. Determined that more information was needed and that Knappe needed to provide next steps. Styers requested Kearns coordinate this request.
4/13/17	Styers, Eckert, Malone & Kearns meet to discuss Knappe's desire for more research, pros, cons, and what CFPUA needed Knappe to provide to improve CFPUA's understanding of the previous paper and next steps.
4/13/17	Kearns to Water Team, inviting team to April 19th meeting with Knappe. Invitees include Flechtner, Styers, Vandermeiden, Heidi Cox (DEQ), McGill, Eckert, and others. Purpose "Been approached by

	Knappe re: legacy & emerging PFAS compounds in our raw water and their fate once they have passed through the Sweeney WTP treatment regime. Due to their persistent nature and potential concentrations in our source water, there is a strong desire to identify the PFAS compounds, their concentrations, and their fate in our treatment plants through a coordinated sampling effort with Detlef's lab. Proposal attached. The scope of this project is such that thorough vetting and buy-in from all Authority levels would be best before anything moves forward."
4/19/17	Water Team Mtg with Knappe. CFPUA staff in attendance (minus Flechtner), as well as Heidi Cox, NC DEQ. Reviewed study results; proposed additional sampling to determine the fate of 1,4-dioxane and perfluoroalkyl substances (PFAS) in the urban water cycle (source -> water system -> distribution -> wastewater -> discharge). Determine fate of 1,4-dioxane & PFAS during ASR; determine possible association of 1,4-dioxane & PFAS with biosolids. Knappe wanted to get other utilities involved in sampling. Knappe wanted his next project to further investigate GenX and its fate and look for potential treatment technologies and to use the research to talk to the state to get it regulated and out of the river.
	Knappe to Styers: "Not enough information to say that you shouldn't drink the water"
	CFPUA staff continues to research GenX and PFOAs and its human health effects. Conflicting information is found; most information stated more information and study is needed to determine what if any health effects are associated with the product.
4/22/17	Knappe forwards abstract (Swedish study) re: GenX toxicity to Kearns, "which purports that GenX is more toxic than PFOA, concentrations in Wilm, Brunswick, & Pender greatly exceed the current health advisory level for PFOA. I think it is important that we push to dramatically reduce inputs of GenX and similar compounds into the CFR".
4/26/17	Eckert requests Chemours NPDES permit from NC DEQ
5/2/17	Eckert discusses issue with Linda Culpepper, DEQ, at ESI mtg. Asks about the process CFPUA would use to get the state's assistance to further investigate and regulate the discharge of new chemicals from Chemours facility. Given the name of a contact in the DEQ Fayetteville Regional Office.
	CFPUA staff draft letter for NC DEQ, will seek board approval.
5/15/17	Star News inquiry to Knappe, forwarded to Kearns & Eckert
6/1/17	CFPUA contacted by StarNews re: Knappe study. Styers discussed with Haggerty and provided answers the next day.
6/5/17	Styers sent email to BOD about upcoming article in StarNews.
6/7/17	CFPUA Exec Committee Mtg: Flechtner brought issue to committee mtg. Styers summarized Knappe report. Mentioned StarNews would be doing article. Committee approved a letter to DEQ, including research paper, requesting DEQ assistance in evaluating the effect of the substance on surface water. No information presented that indicated a health concern. EPA proposed study and they set national drinking water standards. DEQ regulates based on those standards.
6/8/17	StarNews article published.

Interviewees:

Ben Kearns, CFPUA Water Operations Supervisor

John Malone, CFPUA Water Treatment Plant Supervisor

Frank Styers, CFPUA Chief Operations Officer

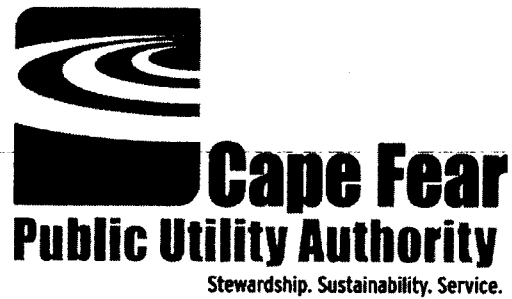
Beth Eckert, CFPUA Environmental Management Director

Jim Flechtner, CFPUA Executive Director

Linda Miles, CFPUA Consulting Attorney
Mike Brown, CFPUA Board Chairman
Dr. Detlef Knappe, NCSU

Prepared by:

Jennifer H Adams, PE, CFPUA Board Vice-Chairman
Robin Smith, JD, Robin Smith Law Office
6/20/17



Review of GenX Response

Agenda

- Background Information on GenX
- EPA/NC DEQ Permitting Process Overview
- Highlights from CFPUA Timeline
- Conclusion & Recommendations



Background on GenX

- One of several new compounds developed to replace PFOA/PFOS
- EPA studies documented health risks associated with PFOA and PFOS
 - Cancer, liver damage, immune effects, etc.
 - First EPA health advisory issued 2009; revised in 2016
- Phaseout of PFOS and PFOA
 - 2000: 3M announced it would stop producing PFOS
 - 2006: EPA reached voluntary agreement with 8 companies to phaseout PFOA by 2015



Regulation of GenX: Clean Water Act

- PFAS not on EPA's list of priority toxic pollutants
- DEQ has classified the Cape Fear River for water supply
 - WQ standards based on protecting river as a water supply source
 - Dischargers meet in-stream water quality standards
- EPA also sets technology-based wastewater limits for categories of industrial dischargers
- If no EPA limit for a pollutant or type of discharge exists, the state water quality permit writer can develop limits on a case by case basis under Clean Water Act criteria.



Regulation of GenX: Safe Drinking Water Act

- EPA has not adopted drinking standards for any PFAS (including PFOA and PFOS)
- 2012: Required 5-year monitoring for PFOA and PFOS in water systems to gather data
- 2016 EPA health advisory for PFOA/PFOS revised to 70 ppt for lifetime exposure
- Health advisory does not apply other PFAS or alternatives like GenX



Drinking Water System

- Treats water to meet national drinking water standards
- Monitors for regulated contaminants and reports results
- Provides notice of standard exceedances
- Voluntary actions in response to EPA health advisories



In Brief

EPA/DEQ: Regulates water quality impacts to the river (standards, wastewater discharge limits)



EPA/DEQ: Regulates drinking water systems; researches health risk; develops drinking water rules



Water System: Operates under drinking water rules (monitoring, treatment, public notices)



Knappe Paper: The Study

- CFPUA partnered in the study to:
 1. Measure concentrations of PFECAs in Cape Fear between Fayetteville Chemours plant and Sweeney WTP
 2. Evaluate effectiveness of water treatment process in removal of PFECAs



Knappe Paper: Results

- Very low levels of PFOA/PFOS in Sweeney raw water
- Higher levels of PFECAs (including GenX)
- GenX concentrations averaged 631 ppt
- Noted lack of information on toxicity of GenX
- Suggested possible need for follow up on discharge control and monitoring



Timeline Highlights

- Summer 2013: Sweeney WTP raw water sampled and analyzed for GenX by Knappe's team
- 2014 to 2015: Knappe's team partners with CFPUA for further studies on
 - Presence of fluorochemicals in the CFR
 - Assess/develop treatment options
- Nov 2016: Knappe paper is published



Timeline Highlights

- April 2017: CFPUA staff discuss Knappe report results and next steps
 - Includes an April 19th water team mtg
 - Knappe reviewed study results
 - Proposed additional sampling through the urban water cycle
 - Knappe wanted research to help with NC DEQ regulatory assistance
- CFPUA staff continue to research GenX, PFOA, health effects
- CFPUA staff request assistance from NC DEQ for further investigation and possible discharge regulation



Timeline Highlights

- May 2017: CFPUA staff draft a letter to NCDEQ
 - Reviewed by Exec Director
 - Reviewed by CFPUA Exec Committee on June 7, 2017
- June 8, 2017: Star News article published



Conclusion & Recommendations

- Given all of the available information, CFPUA staff acted in an appropriate, professional, timely, and scientific manner
 - Data was gathered, studied, and reviewed at appropriate levels
 - Based upon information and facts available to CFPUA at the time, staff moved the issue appropriately through the CFPUA chain of command
- Recommendation to consider a process for releasing “non-routine” sampling results to the public



Summary

- Perfluorochemical alternatives are an emerging class of compounds
 - Little toxicological or environmental data is available
 - Neither US EPA nor NC DEQ has set health or discharge standards
- CFPUA participated in the study to gain scientific knowledge
- CFPUA staff were reviewing and acting upon the available data in an appropriate & scientific manner



- 1) Continue encouraging EPA and DEQ to determine safe / health protective concentration levels of GenX in drinking water.
- 2) Continue encouraging DEQ to determine the relevance/import of NC's IMAC for PFOAs of 1 microgram per liter in groundwater has to drinking water.
- 3) Continue encouraging DEQ and EPA to determine what levels of PFOAs and GenX variants are and will remain in the Cape Fear after the cessation of Chemours discharge, including, but not limited to an assessment of what, if any, release of PFOAs into the Cape Fear are still occurring because of groundwater problems at Chemours.
- 4) If the information provided by EPA and DEQ is not sufficient, determine if CFPUA should hire its own toxicologist/epidemiologist to review and opine upon the safe levels of concentrations of GenX and PFOAs based upon existing studies and otherwise assist CFPUA.
- 5) If EPA and DEQ do not provide an acceptable solution to ensure water quality, determine whether CFPUA could implement some form of additional treatment of its intake water to eliminate/reduce GenX and PFOAs in finished water.
- 6) Remain active and engaged with DEQ and EPA in the Chemours NPDES Permit Renewal process.
- 7) Seek the following additional information from Chemours (perhaps by asking DEQ and EPA to use their authority to obtain):
 - a) Copies of all toxicity studies furnished to DEQ and EPA or otherwise known (this will overlap with documents covered by PRR and FOIA requests to DEQ and EPA, respectively);
 - b) Copies of all studies (or sampling, if any) that Chemours/Dupont has done to determine the efficiency of the removal process; and
 - c) Information and documents regarding the monthly and annual amounts of GenX that Chemours calculates it discharged to the Cape Fear since inception of use.
- 8) Assess what, if any, additional requests for action CFPUA may make of EPA, DEQ, and Chemours.
- 9) Determine what, if any, economic damages, CFPUA has suffered (and/or are likely to suffer in the future) as the result of Chemours/Dupont discharges.

UNREGULATED CONTAMINANTS AND WATER QUALITY REPORTING PROGRAM ENHANCEMENTS

JUNE 23, 2017

Following the recent GenX issue, it makes sense to evaluate ways CFPWA could improve certain processes to ensure customers have access to water quality data. CFPWA runs thousands of compliance tests on its drinking water each year. Moreover, tests on raw water also reveal important information about the quality of our source water. While all this information is public, it is currently not easily accessible to customers.

The EPA Unregulated Contaminant Monitoring Rule (UCMR) identifies and tests for unregulated contaminants in surface waters. Based on test results and potential for health risks, EPA then regulates contaminants by setting standards for public water supplies to meet. CFPWA participates in the UCMR program every five years by testing for certain contaminants and reporting results to EPA. CFPWA includes test results in that year's Water Quality Report, which is a document that describes information about the quality of CFPWA water for the public. The next round of UCMR testing will be in September 2018.

Below is an initial list of steps CFPWA will take to ensure customers can easily reach information about the water supply, as well as steps we will take to ensure water quality information is properly managed.

- Establish a page on the CFPWA web site titled "The Quality of Your Drinking Water"
 - Create a link to any detects of an unregulated contaminant, regardless of whether it is included in UCMR. Advertise new data so customers know to look.
 - Create a link to a rolling 12-month list of water quality test results for compliance
 - Include information about disinfection byproducts, UCMR, source water, FAQs, treatment processes, etc.
 - Include links to EPA, CDC and other sources of health information
- Report UCMR data at a Board meeting, not just through the Water Quality Report
- Issue a press release when new UCMR or other unregulated contaminant test results are available
- Secure Board approval for water study partnerships. After they are complete, bring study results to the next meeting for Board review
- Quickly escalate test data that appears unusual or concerning
- Conduct quarterly or special reviews with the New Hanover County Health Department to discuss water quality trends

This is not to say this a final list of steps CFPWA will take in the wake of GenX. Rather, this is an immediate set of action items that will ensure our customers have proper access to water quality information. Other steps will be developed as lessons from the incident are studied more formally.

~ list/publish on website
→ list of studies
CFPWA is participating in.

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,^{*,†,‡,§} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||} Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

[†]Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

[‡]Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[§]National Exposure Research Laboratory, U.S. Environmental Protection Agency Research, Triangle Park, North Carolina 27711, United States

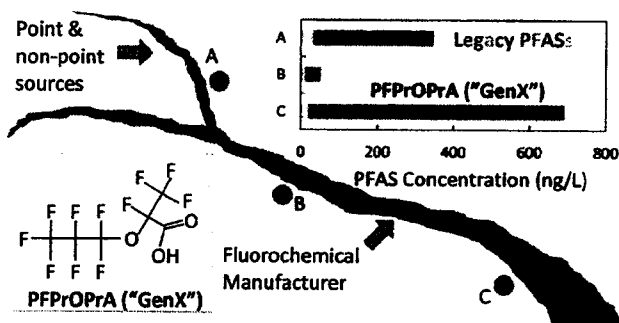
^{||}Cape Fear Public Utility Authority, Wilmington, North Carolina 28403, United States

[⊥]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n = 37$). Six other PFECAs were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain perfluoroalkyl sulfonic acids [$\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$; $n \geq 6$ (PFASs)] and perfluoroalkyl carboxylic acids [$\text{C}_n\text{F}_{2n+1}\text{COOH}$; $n \geq 7$ (PFECAs)] were predominantly used.² Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs^{3,4} has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health

advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.^{5,6} Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.^{7–10} Some fluorinated alternatives were recently identified,^{8,11} but others remain unknown^{12–14} because they are either proprietary or manufacturing byproducts.

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One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.¹¹ Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro-(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxooctanoic) acid (PFO3OA), and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA alternative¹⁵ that has been produced since 2010 with the trade name "GenX". To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,¹⁵ and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),^{16–20} little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C–F bond makes PFASs refractory to abiotic and biotic degradation,²¹ and most water treatment processes are ineffective for legacy PFAS removal.^{22–27} Processes capable of removing PFCAs and PFASs include nanofiltration,²⁸ reverse osmosis,²⁵ ion exchange,^{28,29} and activated carbon adsorption,^{28,29} with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on powdered activated carbon (PAC).

MATERIALS AND METHODS

Water Samples. Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train [raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 20 L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4 °C until use in PAC adsorption experiments (background water matrix characteristics listed in Table S3).

Adsorption Experiments. Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 10–800%

of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 ppm_v) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 µm, BET surface area of 1460 m²/g)³⁰ proven to be effective for PFAS removal in a prior study²⁹ was used at doses of 30, 60, and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

PFAS Analysis. Information about analytical standards and liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods for PFAS quantification is provided in the Supporting Information.

RESULTS AND DISCUSSION

Occurrence of PFASs in Drinking Water Sources. Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1.

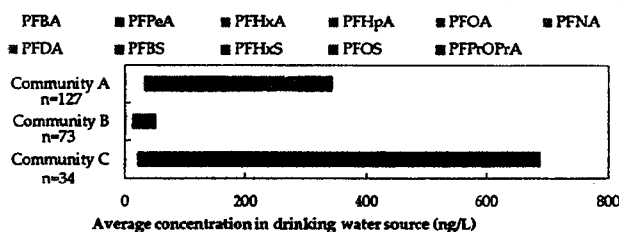


Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean Σ PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,³¹ suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80–85% $C_nF_{2n+1}COOH$; $n = 7–9$) in 2006 to short-chain (76% $C_nF_{2n+1}COOH$; $n = 5–6$) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.

Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLS, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QLS. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.³² However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

Fate of PFASs in Conventional and Advanced Water Treatment Processes. To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.^{22–26} The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSA, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.²⁵ Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400–500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2–113 times greater than that of PFPrOPrA (Figure 2b).

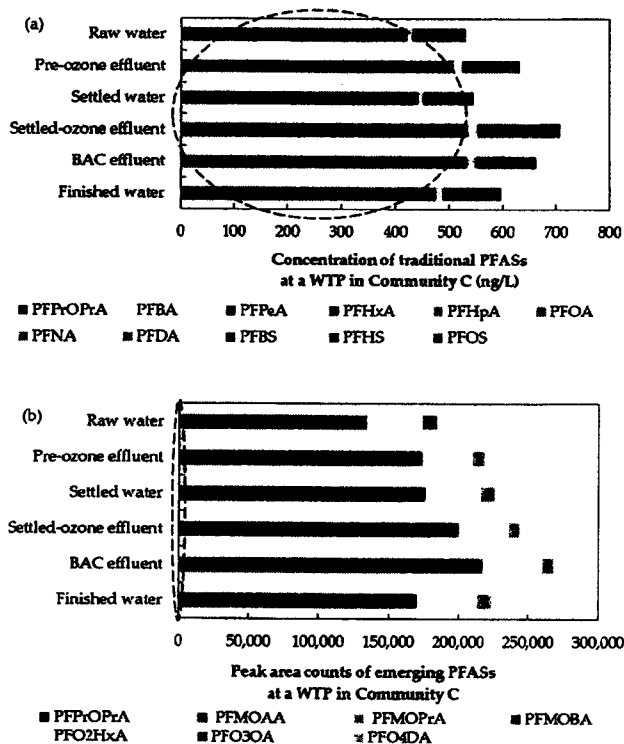


Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QLS were not plotted.

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

Adsorption of PFASs by PAC. PAC can effectively remove long-chain PFCAs and PFSA, but its effectiveness decreases with decreasing PFAS chain length.^{24,25,29} It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥ 7 . At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFASs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous

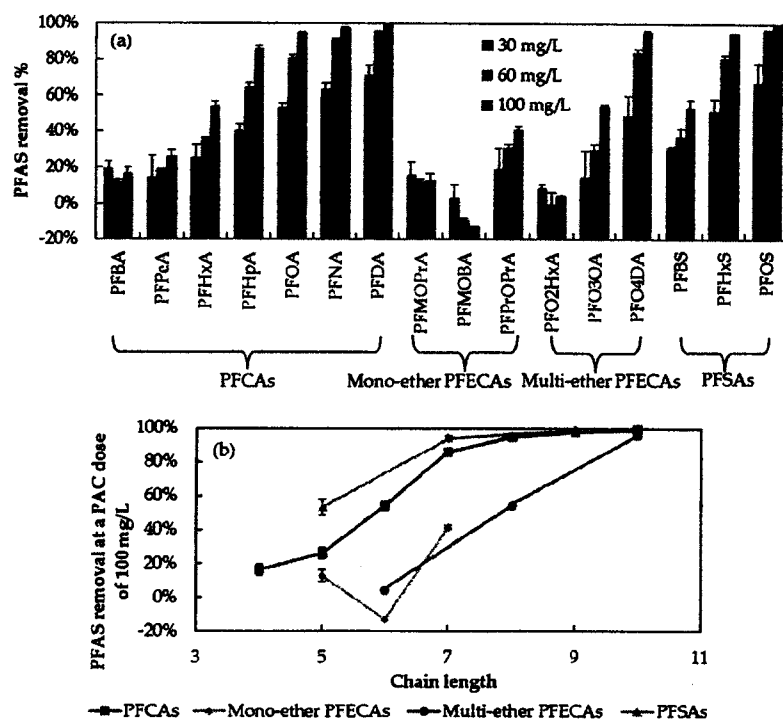


Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ~ 1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

studies.^{24,25,29} PFECAs exhibited adsorbabilities lower than those of PFCAs of the same chain length (e.g., PFMOBA < PFHxA), suggesting that the replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional CF_2 groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA \sim PFO2HxA, PFPrOPrA \sim PFO3OA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMOBA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFECA removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: msun8@unc.edu. Phone: 704-687-1723.

ORCID[®]

Mei Sun: 0000-0001-5854-9862

Notes

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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Adams, Jennifer H

From: Mike McGill <mike@waterpio.com>
Sent: Thursday, June 15, 2017 7:15 PM
To: Adams, Jennifer H
Subject: Mike McGill here. Re: MEDIA ALERT: Statement from CFPUA Board Chairman

Jennifer,

I hope this finds you well. I saw in Mike Brown's statement that you are leading the review of CFPUA's communications on the GenX matter.

I have significant information for you to consider about my involvement and it concerns the circumstances of my departure from CFPUA. I put two and two together tonight, thanks to Mike's statement.

Earlier in March of 2017, I had made it known we needed to have a gameplan to communicate Dr. Knappe's findings in a previous conversation with Beth Eckert (who is aces).

On March 30, 2017, I was placed on a Performance Improvement Plan based on a false charge that I was rude to a customer. Despite TA Loving writing a letter on my behalf about the sanity of the customer in question, I was put on what was basically a "no tolerance" order.

I continue to move through with my work. On April 17, I was informed that the final firing process for me was beginning based on an email I had written the previous week. It was a routine email providing a pro and con breakdown of a radio interview request from WHQR. (I have all documents.)

After a kangaroo court meeting on the 18th, I was walked out the door on April 19th. April 19 was the morning Dr. Knappe visited CFPUA.

I would have been in the Water Team meeting with Dr. Knappe later that morning. I would have again relayed the need to inform the public about GenX. The timing of my firing is not a coincidence.

I forced my way out of being fired and worked out a settlement over the next couple of days, finally signing a handwritten resignation on April 21. The reason: "philosophical differences".

However, it is clear now that Jim wanted me gone from CFPUA before the meeting with Knappe on April 19th. He used trumped up and false charges to make it happen.

I will give you all of the details about my departure, including all documentation of my "crimes". I also tape recorded the kangaroo court meeting on the 18th for cover. I also have a recording of the meeting on 19th but it might have some gaps.

Please contact me by phone whenever you'd like a 910-622-8472. I spoke to the media about my real departure off the record back in April because several reporters wanted to go for my job. They wanted the full rundown of my leaving but they could only have it if I went off-the-record.

I really don't want a public record of my this at this time. Media outlets have told me CFPUA might as well hand over its email server and I'm still getting my business underway.

Mike McGill

On Jun 15, 2017, at 4:09 PM, Kevin Wuzzardo <kwuzzardo@wwaytv3.com> wrote:

Kevin Wuzzardo

News Director

WWAY-TV, LLC

o: 910-763-0979

a: 615 N. Front St., Wilmington, NC 28401

w: wwaytv3.com e: kwuzzardo@wwaytv3.com



----- Forwarded Message -----

Subject: Re: MEDIA ALERT: Statement from CFPUA Board Chairman

Date: Thu, 15 Jun 2017 19:55:20 +0000

From: Michael Brown <Michael.Brown@cfpua.org>

To: Kevin Wuzzardo <kwuzzardo@wwaytv3.com>

Kevin,

CFPUA staff received the initial findings from the NC State research team leading the original study on May 3, 2016. At that point, it is my understanding that the study was still underway. The reason for the review is to establish a full and credible accounting of all of the information that was available at each step of the process.

As previously stated, the results of the Board's internal review will be shared with the public as soon as possible.

Regards,
Mike Brown

From: Kevin Wuzzardo <kwuzzardo@wwaytv3.com>

Sent: Thursday, June 15, 2017 3:49:32 PM

To: Michael Brown

Subject: Re: MEDIA ALERT: Statement from CFPUA Board Chairman

Mike,

Are you saying CFPUA knew of the presence of GenX in the water supply in May 2016?

Thanks
KEVIN

Kevin Wuzzardo

Sent from my iPhone

On Jun 15, 2017, at 3:46 PM, Michael Brown <Michael.Brown@cfpua.org> wrote:

**STATEMENT FROM MIKE BROWN, CHAIRMAN OF THE BOARD, CAPE FEAR PUBLIC UTILITY AUTHORITY
REGARDING GENX:**

"The role of the CFPUA is to provide drinking water that meets or exceeds all state and federal standards so that our drinking water is safe. As a result, we regularly participate in scientific studies of this kind. From the moment we agreed to participate in the NCSU study up until today we have not received any guidance from any regulatory body that we should test for GenX, nor have we received any guidance on effective ways to remove GenX from the water supply. That said, I stand with our colleagues at the state and local levels, and call on Chemours to stop releasing GenX into the Cape Fear River at any level.

As a member of the Wilmington community, I wholeheartedly agree that we, as the CFPUA Board, are obligated to provide transparency in all aspects of this organization, and that the Board of Directors is obligated to fulfill its duty to provide oversight and communicate openly with the public. Therefore, I am going to ask the Board to conduct a review regarding CFPUA's involvement in and communication about the North Carolina State University's study.

We are well aware of the public concern regarding the study and the steps CFPUA followed regarding the discovery of GenX in the Cape Fear River. I will recommend that the review will be led by Jennifer Adams, a chemical engineer and member of the Board. At the conclusion of this review, the Board of Directors will share its findings with the public.

In the interim, the following is an account of events known to me at this time.

CFPUA staff received the initial findings from the NC State research team leading the original study on May 3, 2016. The study progressed, and a final draft was shared with CFPUA staff on September 25, 2016, shortly before the study was published in *Environmental Science and Technology Letters* on November 10, 2016. The study revealed traces of GenX in the Cape Fear River.

The EPA—also an active participant in the NCSU study—through their approvals, allows 1% of the manufacturing waste stream of GenX to be discharged into the river. Because of this, it was not surprising that the study confirmed traces in the water.

Upon confirmation of GenX in the Cape Fear River at the conclusion of this study, CFPUA staff implemented the same due diligence process it uses to study and review all scientific reports and emerging compounds. GenX is one of thousands of unregulated, permitted compounds, and CFPUA willingly participates in studies of these types of compounds on a regular basis.

CFPUA staff worked with the researchers to understand this unregulated, permitted compound, the results of the study, and what they might mean. Based on the information they gathered during this due diligence process, staff determined that additional research was needed to understand the real effects of GenX and potential water treatment options. Staff took their initial learnings and request for additional research to Executive Director Flechtner on March 20, 2017. Staff members continued in their due diligence process from there.

As part of this due diligence process, Dr. Knappe's team came to present to the CFPUA water quality team meeting to present on the study on April 19, 2017, which NCDEQ representatives attended.

Following this initial due diligence phase, staff notified the full board via email on June 5, 2017, and Mr. Flechtner secured permission from the Executive Committee of the Board on June 7, 2017 to send a formal request to NC Department of Environmental Quality (NCDEQ) requesting additional research and regulations for this unregulated, permitted compound. Following Executive Committee approval, Mr. Flechtner submitted the letter via email on June 7, 2017. NCDEQ had been involved in this matter beginning as early as April 19, 2017 and at no time during

the discussion with NCDEQ or EPA did they indicate that this confirmed presence of GenX posed a health risk or a public advisory was necessary.

CFPUA received a response from NCDEQ on June 9. As noted in their correspondence, the NCDEQ formally requested guidance from the EPA, "the sole agency responsible for establishing drinking water standards nationwide. The federal agency has extensive resources necessary to determine the nature, extent and potential impacts of chemicals such as GenX. As such, the North Carolina Department of Environmental Quality is awaiting guidance from the EPA that will provide [NCDEQ] with the information needed to begin developing regulatory limits for GenX.

The Board of Directors can guarantee to the public that CFPWA strictly adheres to all regulations, and can assure its drinking water meets or exceeds all federal and state regulations for safety.

The CFPWA Board of Directors has a responsibility to protect our customers to include full and complete transparency on all aspects of our organization. That's why we are taking proactive steps to review this process. We have a lot of questions, as do our customers. We continue to seek answers, and will deliver updates as quickly as possible.

The board of directors of CFPWA understands that this is a time sensitive matter given public interest. We are committed to being complete, thorough and are committed to releasing results of the review on a timely basis. CFPWA will post updates on its website and social channels. At the conclusion of the Board of Director's independent review of this process, the Board will update the public on its findings."

GenX

Michael Johnson
Chemours Company
Fayetteville Works

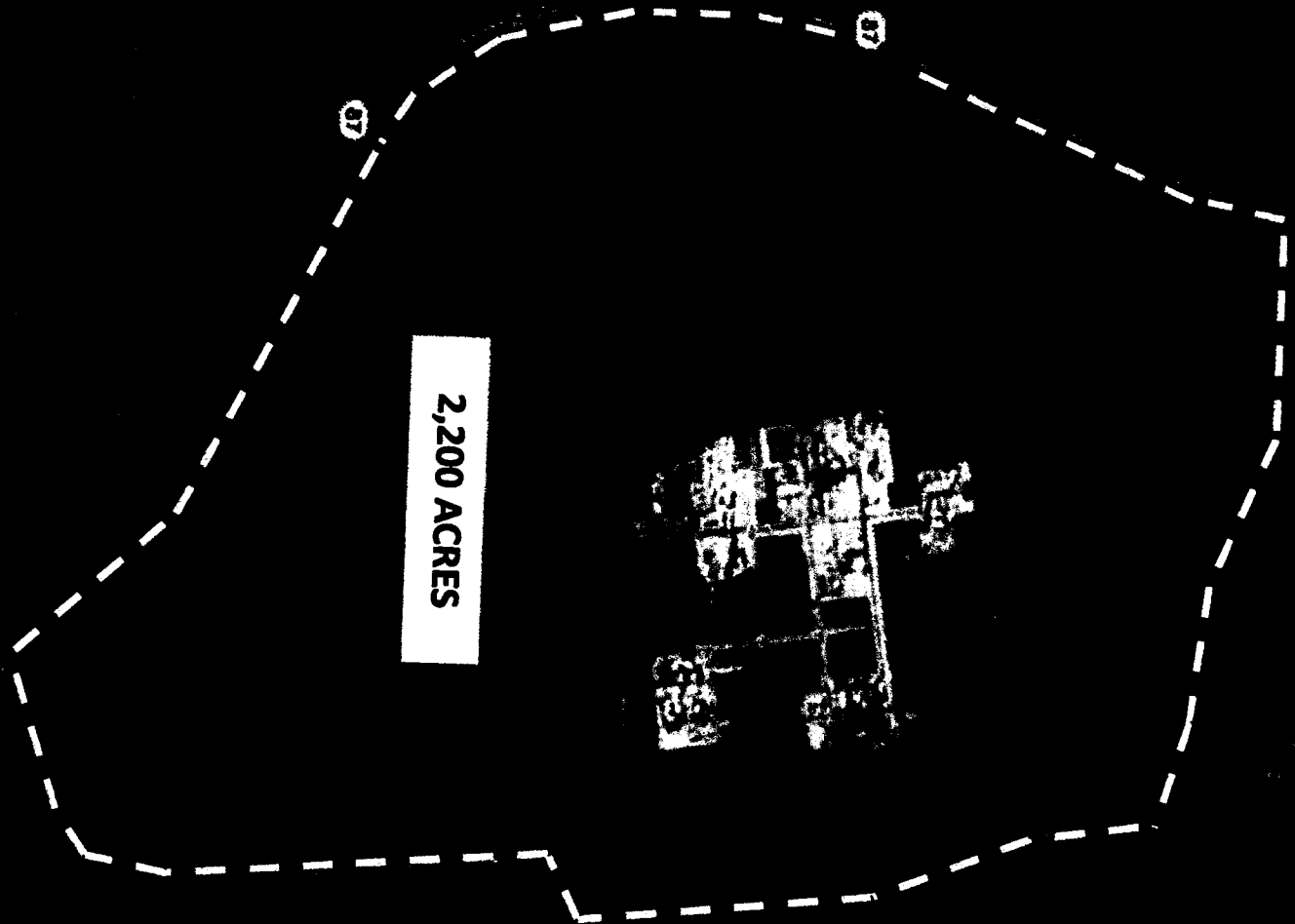
06-12-2017

given to Jim Emerson at NC DED

06-12-2017

1303

2,200 ACRES



CHEMOURS COMPANY - FAYETTEVILLE WORKS

→ Chemmms, where Mark made

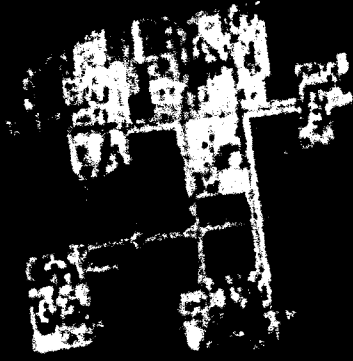
POLYMER
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002

06-12-2017

Chemmms - Nation



RIVER
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OUTFALL
002



87

1303

87

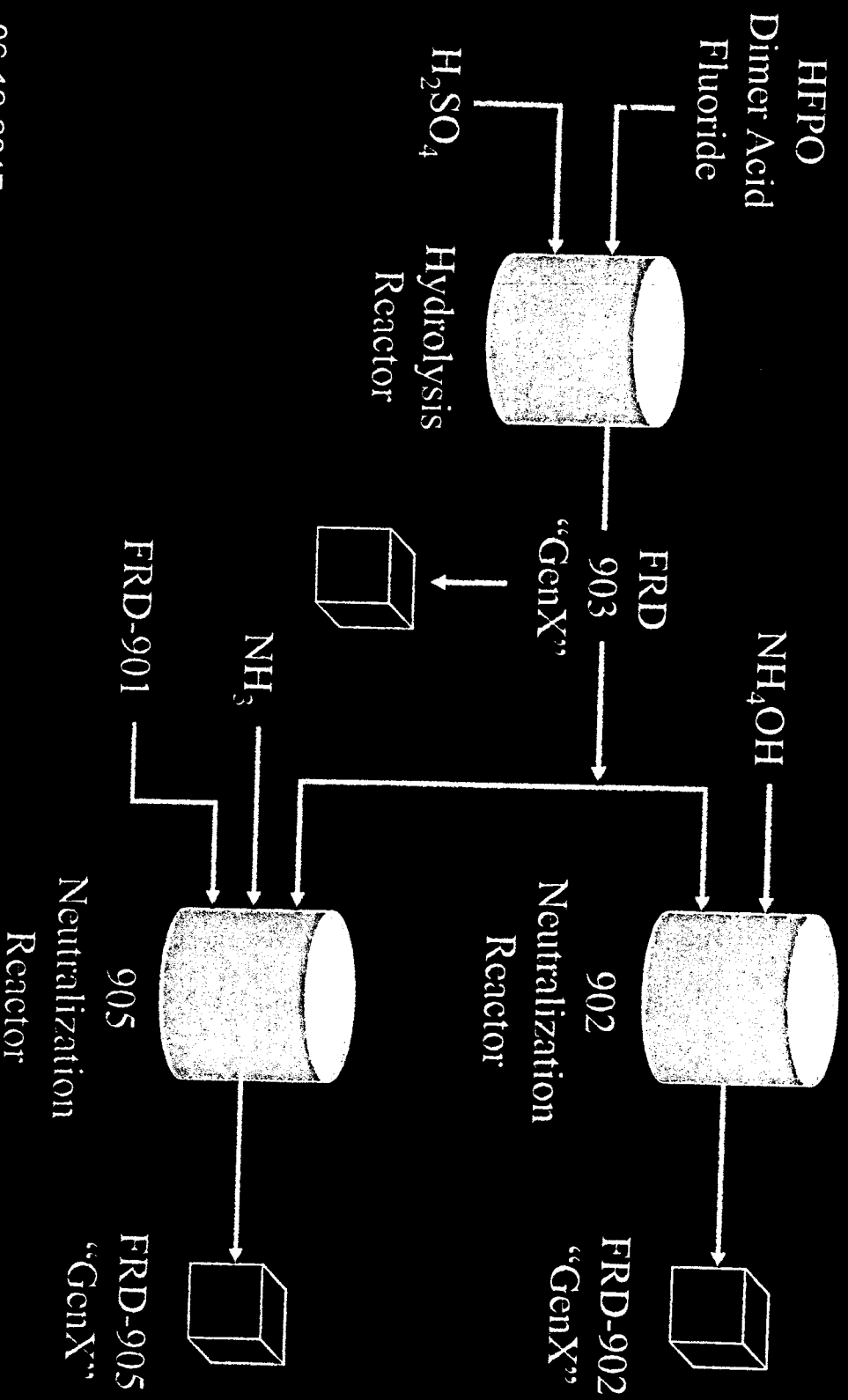
Polymer Processing Aid (PPA) Facility

Family of fluorocarbon surfactants used to produce Chemours™ Teflon® and Kalrex® fluoropolymers, as well as sales to outside producers of fluoropolymers.

Newest line of products are called “Generation X” or “GenX” which replaced APFO.

Initial commercial production was under an USEPA TSCA Consent Order.

PPA Process

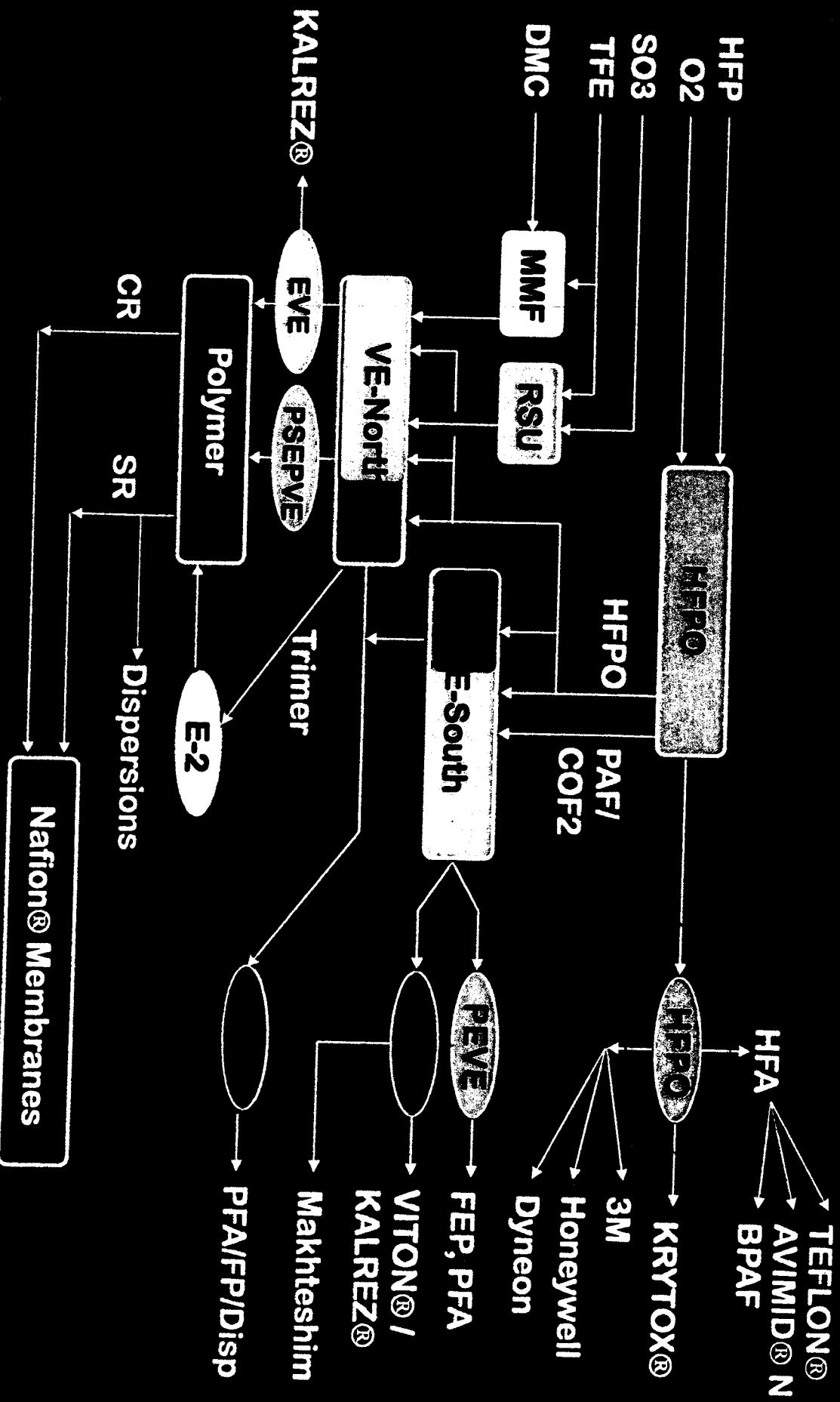


Fluoromonomers

Family of fluorocarbon compounds used to produce DuPont products such as Nafion® membranes, Teflon®, Kalrez®, Krytox®, and Viton®, as well as sales to outside customers.

- Hexafluoropropylene oxide (HFPO)
- Perfluorinated vinyl ethers - PMVE, PEVE, PPVE, EVE, and PSEPVE
- Precursors - MMF, RSU, and Freon® E-2

Fluoromonomers (FPS) / Nafion® Membrane (IXM)



06-12-2017

Fluoromonomers

- Vinyl Ethers Process generates HFPO Dimer Acid during the PPVE campaign.
- HFPO Dimer Acid (FRD-902) is the raw material used to produce the GenX products.
- HFPO Dimer Acid abatement system was installed/started in November 2013.
- Since that start-up it is estimated the HFPO Dimer Acid concentration during normal PPVE operation to be 100 ppt at Lock & Dam No. 1

Questions?

06-12-2017

Beth Eckert

From: Gregson, Jim <jim.gregson@ncdenr.gov>
Sent: Monday, June 12, 2017 6:25 PM
To: Beth Eckert
Subject: Fwd: chemours pres
Attachments: Chemours GenX.pptx; ATT00001.htm

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section
Division of Water Resources
Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405



Email correspondence to and from this address is subject to the North Carolina Public Records Law and may be disclosed to third parties.

Begin forwarded message:

From: "Young, Sarah" <sarah.young@ncdenr.gov>
To: "Karoly, Cyndi" <cyndi.karoly@ncdenr.gov>, "Allen, Trent" <trent.allen@ncdenr.gov>, "Gregson, Jim" <jim.gregson@ncdenr.gov>
Cc: "Culpepper, Linda" <linda.culpepper@ncdenr.gov>
Subject: chemours pres

Sarah M. Young
Public Information Officer
N.C. Department of Environmental Quality
Division of Coastal Management
919-707-8604 office
sarah.young@ncdenr.gov

Adams, Jennifer H

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Saturday, June 24, 2017 8:56 PM
To: Adams, Jennifer H
Subject: Fwd: Fwd: PFAS paper published
Attachments: PFECAs_Sun_ESTL2016.pdf; PFECAs_Sun_ESTL2016_SI.pdf

Hi Jennifer,

I noticed the following statement on the WWAY web page:

According to the report, on Nov. 23, 2016, Dr. Knappe emailed the published paper to multiple people within the NC Department of Environmental Quality and various cities, but not CFPUA, even though his email specifically mentioned the impacts on Wilmington's water supply.

While this sentence is correct for the November 23, 2016 email, it does not fully characterize how I shared the information about the published paper. On November 19, 2016, I sent the email below and attachments to the co-authors of the paper, which included Mike Richardson and Ben Kearns. At the time, I did not realize that Mike Richardson had retired.

As you can see below, I shared my November 19, 2016 email also with Frank Styers on June 16, 2017.

The November 19, 2016 email does not appear in your timeline. Can you please comment on this matter? I recognize that I should have shared the paper with people higher up in the CFPUA organization, but to characterize my information sharing as one where I left out CFPUA is incorrect.

A smaller error, but one that may still be important, is that my May 3, 2016 email was addressed to Mike Richardson only, not to Ben Kearns. This should be corrected as well because in one of my responses to a reporter I stated that my first e-mail contact with Ben Kearns was not until September 6, 2016 (based on a search of my outbox). I want to make sure things are characterized accurately.

In the end, I hope the focus can be back on Chemours and on clean drinking water. I find this side story quite a distraction. I have great respect for the CFPUA staff, and without their cooperation, especially that of Ben Kearns and Mike Richardson, the fluorochemical pollution may very well still be undiscovered.

Regards,
Detlef

----- Forwarded Message -----

Subject: Fwd: PFAS paper published
Date: Fri, 16 Jun 2017 08:30:53 -0400
From: Detlef Knappe <knappe@ncsu.edu>
To: Frank Styers <frank.styers@cfpua.org>

Frank,

Here is the email I sent when the paper was accepted.

Detlef

----- Forwarded Message -----

Subject:PFAS paper published

Date:Sat, 19 Nov 2016 13:36:29 -0500

From:Detlef Knappe <knappe@ncsu.edu>

To:Chris Smith <chris.smith@faypwc.com>, Chad Ham <chad.ham@faypwc.com>, Mick Noland <mick.noland@faypwc.com>, Michael Richardson <Michael.Richardson@cfpua.org>, Kearns, Ben <Ben.kearns@cfpua.org>, Adam Pickett <apickett@pittsboronc.gov>, Mei Sun <msun8@uncc.edu>

Hello everyone,

I wanted to let you know that the ES&T Letters paper is now published at

<http://pubs.acs.org/doi/abs/10.1021/acs.estlett.6b00398>

The paper and supporting information are also attached to this email.

If you would like to discuss, please let me know! It is possible that this article will generate some news coverage.

Thank you for all of your cooperation with the sample collection,
Detlef

--

Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering

North Carolina State University

Campus Box 7908

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>



Chemours™

The Chemours Company
Fluoroproducts
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

910-483-4681
chemours.com

**CERTIFIED MAIL ARTICLE NUMBER 7002 0860 0006 9104 7828
RETURN RECEIPT REQUESTED**

April 27, 2016

Ms. Wren Thedford
NCDEQ Division of Water Resources
NPDES Unit
1617 Mail Service Center
Raleigh, North Carolina 27699-1617

RECEIVED/NCDEQ/DWR

MAY 03 2016

SUBJECT: NPDES Permit Renewal Application
NPDES Permit No. NC0003573

Water Quality
Permitting Section

Dear Ms. Thedford:

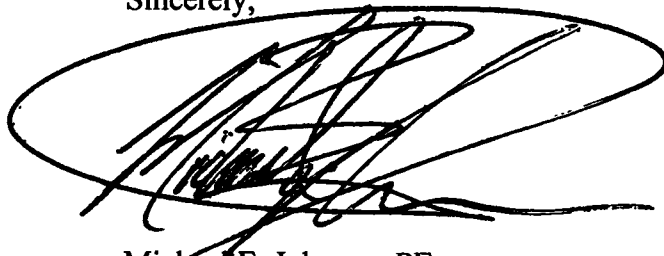
The Chemours Company – Fayetteville Works is requesting renewal of NPDES Wastewater Discharge Permit No. NC0003573. Since the issuance of the last permit, the ownership of this facility changed from the DuPont Company to The Chemours Company FC, LLC. Also, two separate companies, Kuraray America Inc. and the DuPont Company, are operating manufacturing units and are treating and discharging their wastewaters under the Chemours' NPDES Permit.

Enclosed are the original and two copies of the General Information Form 1 (Form 3510-1), Wastewater Discharge Information Form 2C (Form 3510-2C), and additional required supporting documentation for renewal of the subject permit by the NC Division of Water Resources.

Included in the permit application are the following supplemental information documents: Sludge Management Plan, Current Facility Wastewater Management, Current Facility Operating Conditions, Alternate Application Schedule for §316(b) of the Clean Water Act, Elimination of Monitoring Requirement for PFOA, and the non-reporting of bis(chloromethyl) ether.

If you have any questions or need additional information, please contact me at (910) 678-1155.

Sincerely,



Michael E. Johnson, PE
Environmental Manager

Enclosures

CONTINUE ON REVERSE

CONTINUED FROM THE FRONT

VII SIC CODES (4-digit, in order of priority)

A FIRST				B SECOND			
C	7	2869	(specify) INDUSTRIAL ORGANIC CHEMICALS	C	7	3083	(specify) LAMINATED PLASTICS PLATE, SHEET, AND PROFILE SHAPES
15	16	17	18	15	16	17	18
C THIRD				D FOURTH			
C	7	3081	(specify) UNSUPPORTED PLASTICS FILM AND SHEET NOTE: Kuraray Butacite Butacite® and SentryGlas® sheeting process units	C	7	2821	(specify) PLASTIC MATERIALS AND RESINS NOTE: DuPont PVF resin process units
15	16	17	18	15	16	17	18

VIII OPERATOR INFORMATION

A NAME															B. Is the name listed in Item VIII-A also the owner?	
C	8	The Chemours Company FC, LLC													<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO	
15	16															

C. STATUS OF OPERATOR (Enter the appropriate letter into the answer box if "Other," specify)

F = FEDERAL	M = PUBLIC (other than federal or state)	P	(specify)	D PHONE (area code & no)
S = STATE	O = OTHER (specify)			A (302) 773-1000
P = PRIVATE				
				15 16 17 18 19 20 21 22 23 24

E STREET OR P O BOX

1007 Market Street																								

F CITY OR TOWN

F CITY OR TOWN															G STATE		H ZIP CODE		IX INDIAN LAND	
C	B	Wilmington													DE		19898		Is the facility located on Indian lands? <input type="checkbox"/> YES <input checked="" type="checkbox"/> NO	
15	16																			

X EXISTING ENVIRONMENTAL PERMITS

A NPDES (Discharges to Surface Water)										D PSD (Air Emissions from Proposed Sources)									
C	T	I	NC0003573							C	T	I	NC Title V Permit 03735						
9	N									9	P								
15	16	17	18	19	20	21	22	23	24	15	16	17	18	19	20	21	22	23	24
B UIC (Underground Injection of Fluids)										E OTHER (specify)									
C	T	I	N/A							C	T	I	WQ0035431 (specify) Land Application Permit						
9	U									9									
15	16	17	18	19	20	21	22	23	24	15	16	17	18	19	20	21	22	23	24
C RCRA (Hazardous Wastes)										E OTHER (specify)									
C	T	I	NCD047368642							C	T	I							
9	R									9									
15	16	17	18	19	20	21	22	23	24	15	16	17	18	19	20	21	22	23	24

XI MAP

Attach to this application a topographic map of the area extending to at least one mile beyond property boundaries. The map must show the outline of the facility, the location of each of its existing and proposed intake and discharge structures, each of its hazardous waste treatment, storage, or disposal facilities, and each well where it injects fluids underground. Include all springs, rivers, and other surface water bodies in the map area. See instructions for precise requirements.

XII. NATURE OF BUSINESS (provide a brief description)

The Chemours Company - Fayetteville Works (formerly the DuPont Company - Fayetteville Works) is a fluorinated chemicals manufacturer situated on a 2,200-acre property in northwestern Bladen County, NC.

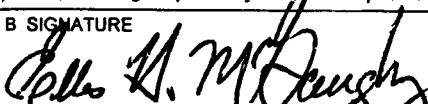
The Chemours' products produced at the facility include fluorinated monomers and fluorinated vinyl ethers, Nafion™ membranes and dispersion, and fluoropolymer processing aids. Chemours operates two natural gas / fuel oil-fired boilers, which provides steam for the entire facility.

Also located at this facility are two tenant companies: Kuraray America Inc. and the DuPont Company. Kuraray operates the Butacite® polyvinyl butyral (PVB) thermoplastic sheet and resin manufacturing unit and the SentryGlas® ionoplast interlayer manufacturing unit. DuPont operates two polyvinyl fluoride (PVF) resin manufacturing units.

Chemours receives and treats all of the Kuraray and DuPont process wastewater, sanitary wastewater, and contact stormwater in the Chemours' owned and operated wastewater treatment plant, and discharges that treated wastewater through Outfall 001 under the Chemours' NPDES Wastewater Discharge Permit (Permit No. NC0003573). The Kuraray and DuPont non-contact cooling waters and stormwaters are discharged through Outfall 002 under the Chemours' NPDES Wastewater Discharge Permit.

XIII CERTIFICATION (see instructions)

I certify under penalty of law that I have personally examined and am familiar with the information submitted in this application and all attachments and that, based on my inquiry of those persons immediately responsible for obtaining the information contained in the application, I believe that the information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment.

A. NAME & OFFICIAL TITLE (type or print)	B. SIGNATURE	C. DATE SIGNED
Ellis H. McGaughey - Plant Manager		4/27/2016

COMMENTS FOR OFFICIAL USE ONLY

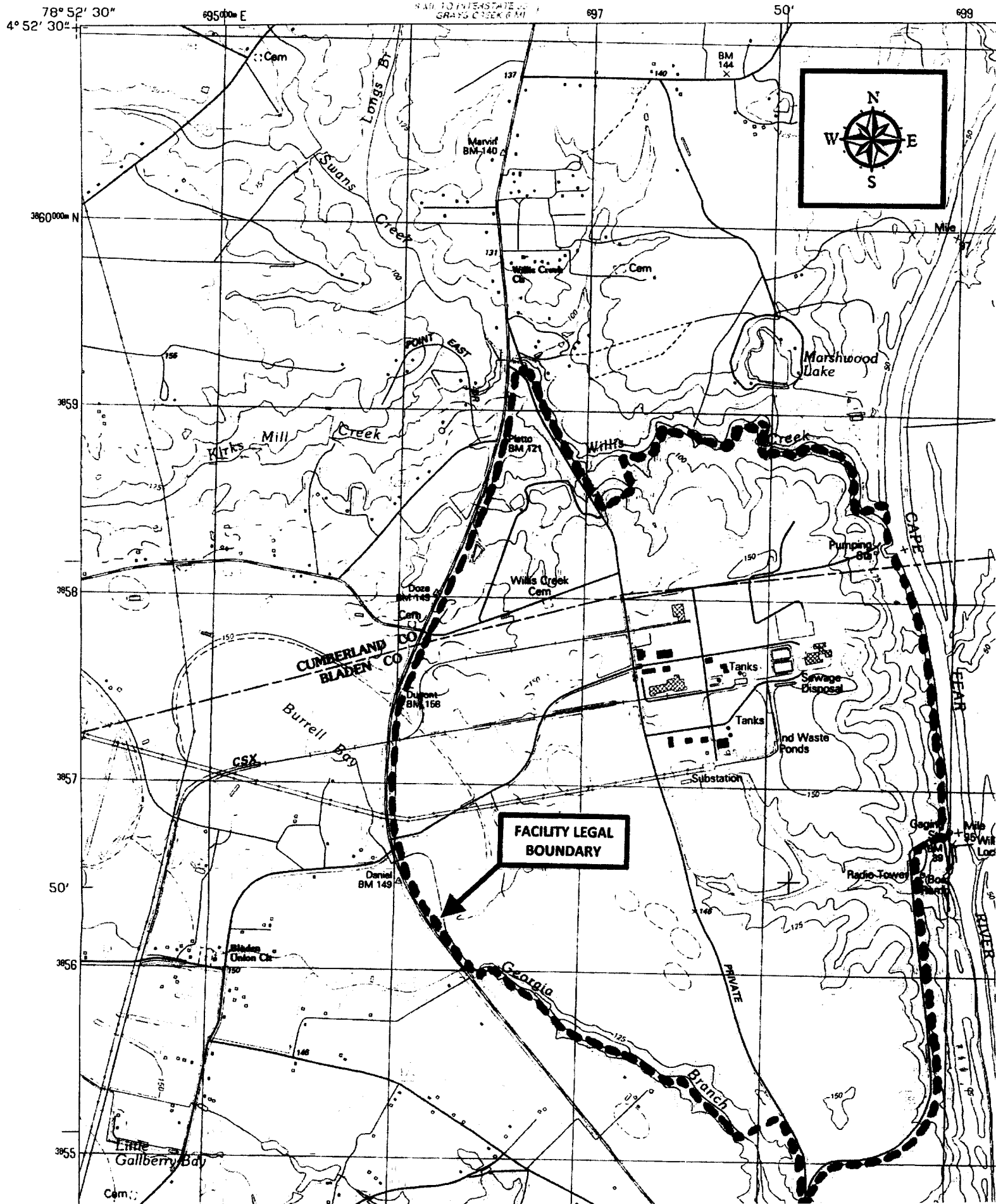
C																								
C																								
15	16																							25

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

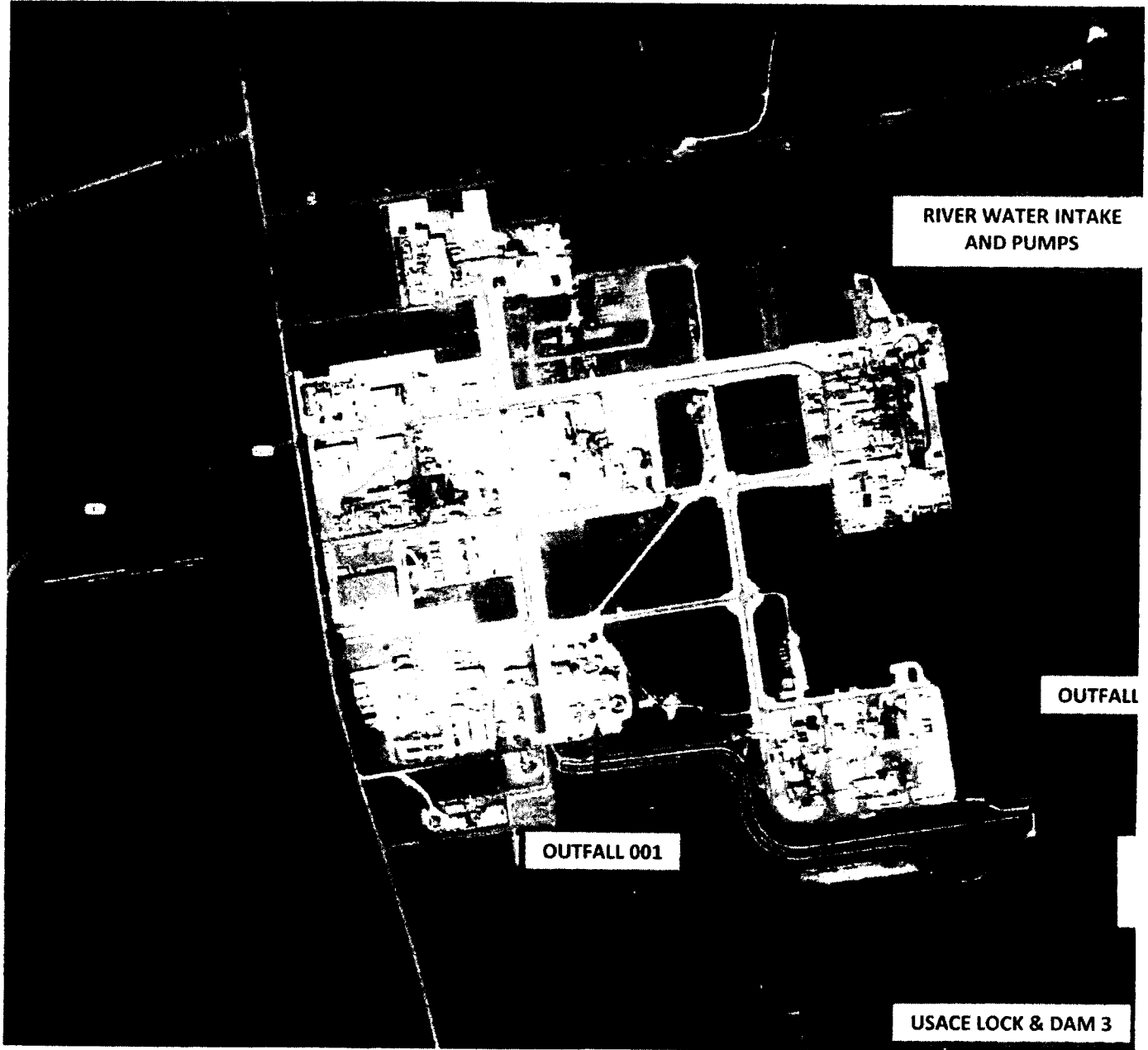
DUART QUADRANGLE
NORTH CAROLINA
7.5 MINUTE SERIES (TOPOGRAPHIC)
SE/4 SAINT PAULS 15' QUADRANGLE

DEI

525' N NW
1/4 (1/4 MILE)

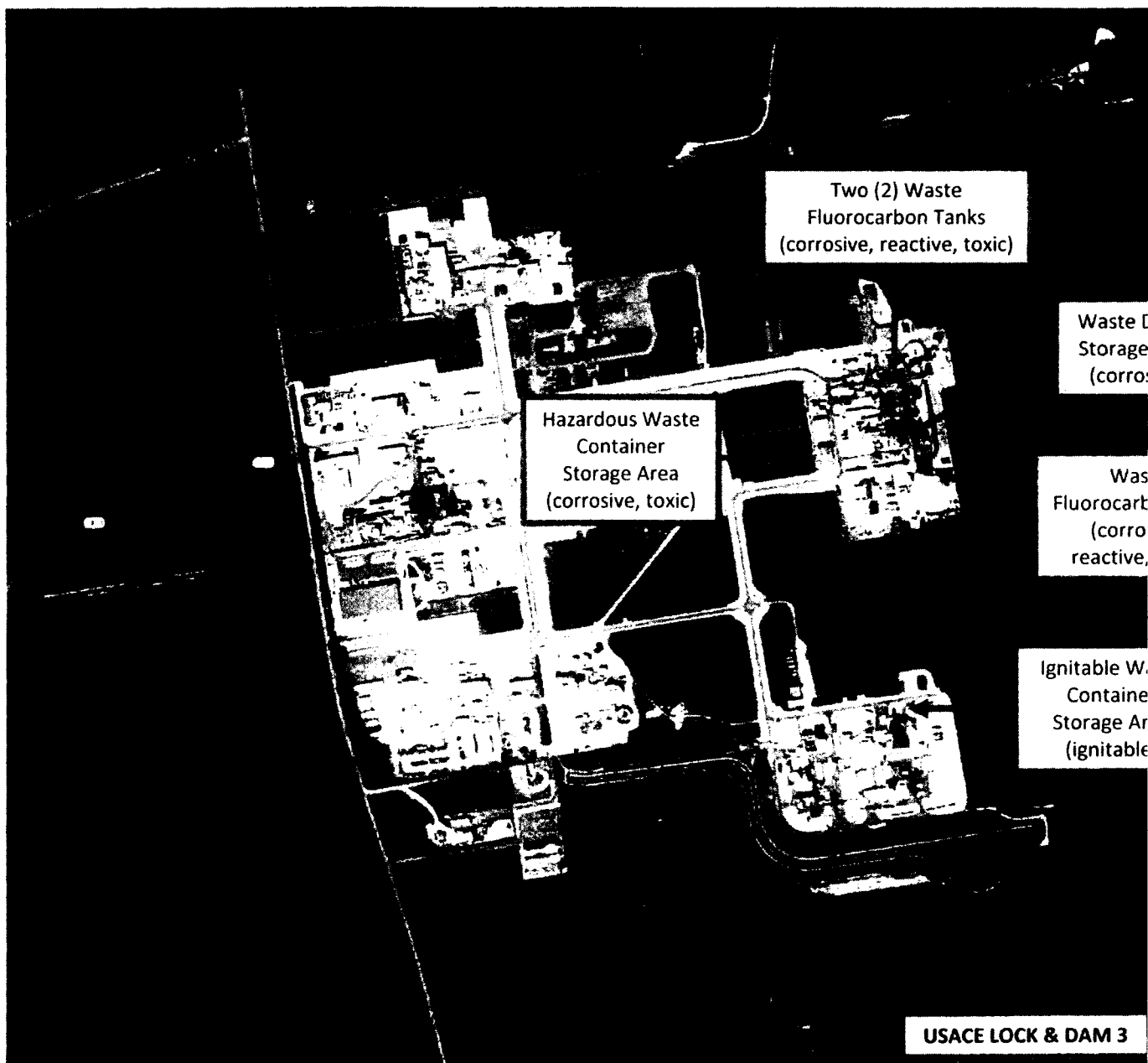


**CHEMOURS COMPANY – FAYETTEVILLE WORKS
LOCATIONS OF INTAKE AND DISCHARGE STRUCTURES**



CHEMOURS COMPANY – FAYETTEVILLE WORKS

LOCATIONS OF HAZARDOUS WASTE MANAGEMENT FACILITIES





EPA ID NUMBER (copy from Item 1 of Form 1)

NCD 047 368 642

Form Approved.
OMB No. 2040-0086
Approval expires 3-31-98.

Please print or type in the unshaded areas only.

FORM
2C
NPDESU.S. ENVIRONMENTAL PROTECTION AGENCY
APPLICATION FOR PERMIT TO DISCHARGE WASTEWATER
EXISTING MANUFACTURING, COMMERCIAL, MINING AND SILVICULTURE OPERATIONS
Consolidated Permits Program

I. OUTFALL LOCATION

For each outfall, list the latitude and longitude of its location to the nearest 15 seconds and the name of the receiving water.

A. OUTFALL NUMBER (/s/)	B. LATITUDE			C. LONGITUDE			D. RECEIVING WATER (name)
	1 DEG	2 MIN	3 SEC	1 DEG	2 MIN	3 SEC	
001	34.00	50.00	22.93	-78.00	50.00	11.47	Cape Fear River
002	34.00	50.00	21.58	-78.00	49.00	25.70	Cape Fear River

II. FLOWS, SOURCES OF POLLUTION, AND TREATMENT TECHNOLOGIES

A. Attach a line drawing showing the water flow through the facility. Indicate sources of intake water, operations contributing wastewater to the effluent, and treatment units labeled to correspond to the more detailed descriptions in Item B. Construct a water balance on the line drawing by showing average flows between intakes, operations, treatment units, and outfalls. If a water balance cannot be determined (e.g., for certain mining activities), provide a pictorial description of the nature and amount of any sources of water and any collection or treatment measures.

B. For each outfall, provide a description of: (1) All operations contributing wastewater to the effluent, including process wastewater, sanitary wastewater, cooling water, and storm water runoff; (2) The average flow contributed by each operation; and (3) The treatment received by the wastewater. Continue on additional sheets if necessary.

1. OUTFALL NO. (/s/)	2. OPERATION(S) CONTRIBUTING FLOW		3. TREATMENT		
	a. OPERATION (/s/)	b. AVERAGE FLOW (include units)	a. DESCRIPTION	b. LIST CODES FROM TABLE 2C-1	
001	Chemours Manufacturing Processes	159,361 gal/day	BIOLOGICAL WASTEWATER TREATMENT PLANT		
	Kuraray Butacite Mfg Process	555,657 gal/day	(1) Influent Sump	1-C	
	Kuraray SentryGlas Mfg Process	0 gal/day	(2) Equalization with mixing and aeration	1-C	3-E
	DuPont PVF Mfg Processes	211,654 gal/day	(3) Emergency Retention Tank	1-C	
	Demin Water Neutralized Regenerate	75,000 gal/day	(4) Pre-Digester Tank	3-E	
	Sanitary Sewer	10,000 gal/day	(5) Activated Sludge Aeration Tank	3-A	
	Process Areas Stormwater	94,216 gal/day	(6) Clarification (3 clarifiers in parallel)	1-C	
	TOTAL INFLOW TO WWTP	1,205,888 gal/day			
	Evaporation from WWTP Operations	50,000 gal/day	BIOLOGICAL SLUDGE (SOLIDS) MANAGEMENT		
	Evaporation from Sludge Drying	19,943 gal/day	(1) Dissolved Air Flotation	5-J	
	Water Content of Landfilled Sludge	2,433 gal/day	(2) Rotary Filter	5-C	
	OUTFALL 001 - TOTAL EFFLUENT	1,133,452 gal/day	(3) Sludge Filter Press	4-R	
			(4) Sludge Steam-Heated Dryers	5-M	
			(5) Disposal at Off-site Landfill	5-Q	
002	Outfall 001 Treated Effluent	1,133,452 gal/day			
	Non Contact River Water	23,057,845 gal/day			
	Non contact filtered water	1,923,328 gal/day			
	Stormwater	211,509 gal/day			
	Sediment Removal	50,000 gal/day			
	Boiler Condensate Slowdown	324,000 gal/day			
	OUTFALL 002 - TOTAL EFFLUENT	26,813,133 gal/day	Discharge to surface water (Cape Fear River)	4-A	

OFFICIAL USE ONLY (effluent guidelines sub-categories)

CONTINUED FROM THE FRONT

C Except for storm runoff, leaks, or spills, are any of the discharges described in Items II-A or B intermittent or seasonal?

☐ YES (complete the following table)

☒ NO (go to Section III)

1 OUTFALL NUMBER (list)	2 OPERATION(S) CONTRIBUTING FLOW (list)	3 FREQUENCY		4 FLOW					
		a DAYS PER WEEK (specify average)	b MONTHS PER YEAR (specify average)	a FLOW RATE (in mgd)		B TOTAL VOLUME (specify with units)		C DURATION (in days)	
				1 LONG TERM AVERAGE	2 MAXIMUM DAILY	1 LONG TERM AVERAGE	2 MAXIMUM DAILY		

III. PRODUCTION

A. Does an effluent guideline limitation promulgated by EPA under Section 304 of the Clean Water Act apply to your facility?

☒ YES (complete Item III-B)

☐ NO (go to Section IV)

B. Are the limitations in the applicable effluent guideline expressed in terms of production (or other measure of operation)?

☐ YES (complete Item III-C)

☒ NO (go to Section IV)

C. If you answered "yes" to Item III-B, list the quantity which represents an actual measurement of your level of production, expressed in the terms and units used in the applicable effluent guideline, and indicate the affected outfalls

1. AVERAGE DAILY PRODUCTION			2. AFFECTED OUTFALLS (list outfall numbers)
a. QUANTITY PER DAY	b. UNITS OF MEASURE	c. OPERATION, PRODUCT, MATERIAL, ETC. (specify)	

IV. IMPROVEMENTS

A. Are you now required by any Federal, State or local authority to meet any implementation schedule for the construction, upgrading or operations of wastewater treatment equipment or practices or any other environmental programs which may affect the discharges described in this application? This includes, but is not limited to, permit conditions, administrative or enforcement orders, enforcement compliance schedule letters, stipulations, court orders, and grant or loan conditions.

☐ YES (complete the following table)

☒ NO (go to Item IV-B)

1. IDENTIFICATION OF CONDITION AGREEMENT, ETC.	2. AFFECTED OUTFALLS		3. BRIEF DESCRIPTION OF PROJECT	4. FINAL COMPLIANCE DATE	
	a NO	b SOURCE OF DISCHARGE		a REQUIRED	b PROJECTED

B. OPTIONAL: You may attach additional sheets describing any additional water pollution control programs (or other environmental projects which may affect your discharges) you now have underway or which you plan. Indicate whether each program is now underway or planned, and indicate your actual or planned schedules for construction

☐ MARK "X" IF DESCRIPTION OF ADDITIONAL CONTROL PROGRAMS IS ATTACHED

EPA I.D. NUMBER (copy from Item 1 of Form 1)

NCD 047 368 642

CONTINUED FROM PAGE 2

V INTAKE AND EFFLUENT CHARACTERISTICS**A B. & C:** See instructions before proceeding - Complete one set of tables for each outfall - Annotate the outfall number in the space provided.

NOTE: Tables V-A, V-B, and V-C are included on separate sheets numbered V-1 through V-9.

D. Use the space below to list any of the pollutants listed in Table 2C-3 of the instructions, which you know or have reason to believe is discharged or may be discharged from any outfall. For every pollutant you list, briefly describe the reasons you believe it to be present and report any analytical data in your possession.

1. POLLUTANT	2. SOURCE	1. POLLUTANT	2. SOURCE
None of the pollutants listed in Table 2C-3 are believed to be present in the wastewater discharge from this site.			

VI POTENTIAL DISCHARGES NOT COVERED BY ANALYSIS

Is any pollutant listed in Item V-C a substance or a component of a substance which you currently use or manufacture as an intermediate or final product or byproduct?

☒ **YES** (list all such pollutants below)☐ **NO** (go to Item 11-B)

Antimony
Benzene
1,2-dichloroethane
Methylene chloride
Toluene

CONTINUED FROM THE FRONT

VII. BIOLOGICAL TOXICITY TESTING DATA

Do you have any knowledge or reason to believe that any biological test for acute or chronic toxicity has been made on any of your discharges or on a receiving water in relation to your discharge within the last 3 years?

☒ YES (Identify the tests and describe their purposes below)

☐ NO (go to Section VIII)

The "North Carolina Ceriodaphnia Chronic Effluent Bioassay Procedure" is performed each quarter in accordance with the requirement of condition A(4) of the facility's NPDES Permit. The NCDEQ Division of Water Resources has copies of the Form AT-1 test results that were submitted with the Discharge Monitoring Reports during the period from February 2012 through February 2016.

The quarterly chronic test performed during February 2012, failed for the ceriodaphnia dubia reproduction. The required monthly chronic tests performed in March and April 2012 both passed. No other toxicity test failures occurred during the five-year term of the current permit.

VIII. CONTRACT ANALYSIS INFORMATION

Were any of the analyses reported in Item V performed by a contract laboratory or consulting firm?

☒ YES (List the name, address, and telephone number of, and pollutants analyzed by, each such laboratory or firm below)

☐ NO (go to Section IX)

A NAME	B ADDRESS	C TELEPHONE (area code & no.)	D. POLLUTANTS ANALYZED (list)
TBL	2401 West 5th Street Lumberton, NC 28358	910-738-6190	Chemical Oxygen Demand (COD); Total Organic Carbon (TOC); Total Suspended Solids (TSS); Ammonia (as N); Color; Fecal Coliform; Fluoride; Nitrate-Nitrite (as N); Nitrogen; Total Organic (as N); Oil and Grease; Total Phosphorus (as P); Sulfate (as SO ₄); Surfactants; Total Aluminum; Total Iron; Total Magnesium; Total Manganese; Part C Metals; Cyanide; and Total Phenols; Part C GC/MS - Volatile Compounds; Part C GC/MS - Acid Compounds; Part C GC/MS - Base/Neutral Compounds; Part C GC/MS Fraction - Pesticides

IX. CERTIFICATION

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

A NAME & OFFICIAL TITLE (type or print)

Ellis H. McGaughy - Plant Manager

B PHONE NO. (area code & no.)

(910) 678-1224

C SIGNATURE

Ellis H. McGaughy

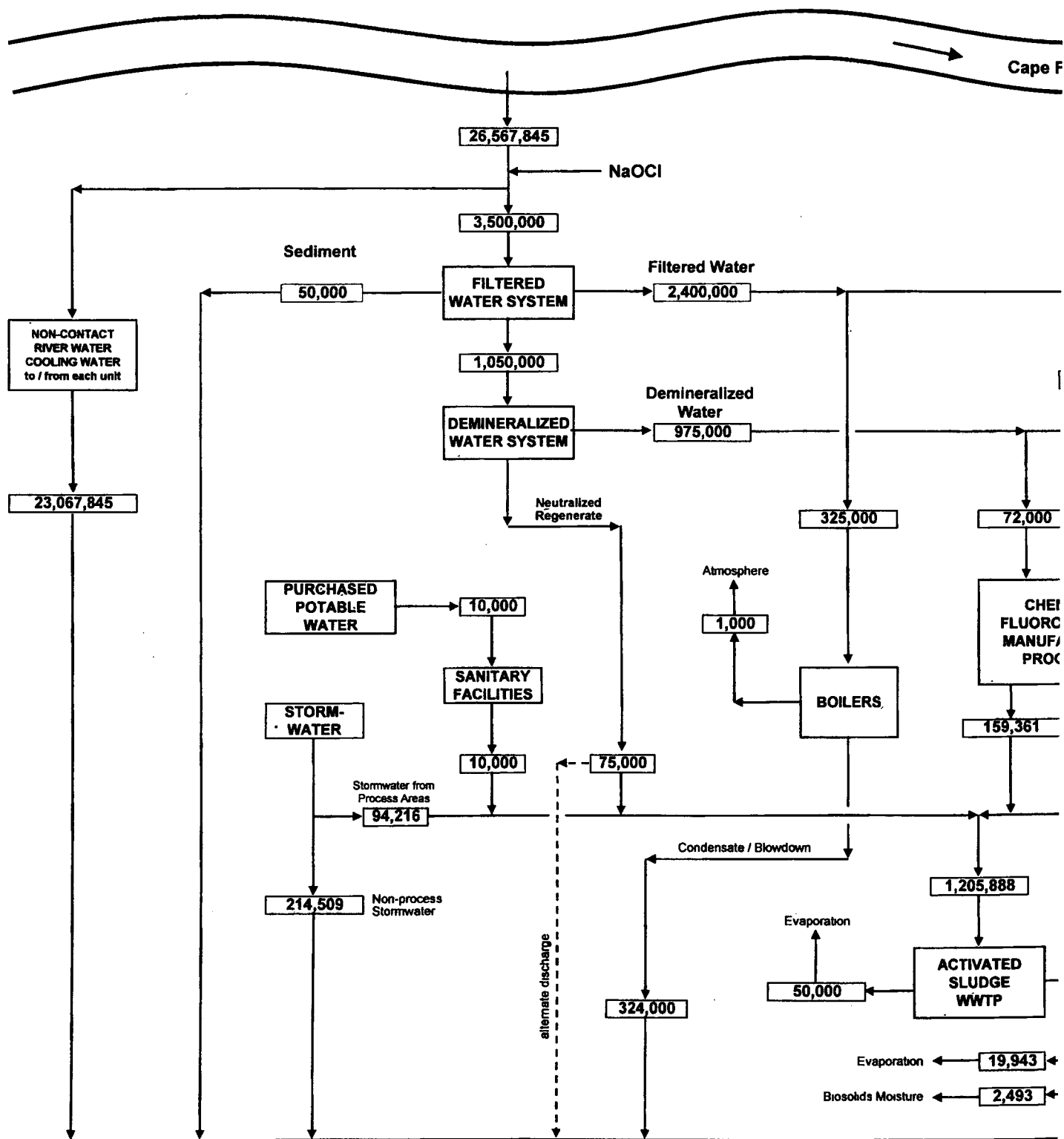
D DATE SIGNED

04/27/2014

Flow Units: Gallons per Day

Basis: (1) All Manufacturing Units operating

(2) Maximum 30-day average of measured flows (2013 - 2015)



PLEASE PRINT OR TYPE IN THE UNSHADED AREAS ONLY. You may report some or all of this information on separate sheets (use the same format) instead of completing these pages
SEE INSTRUCTIONS.

EPA I.D. NUMBER (copy from Item 1 of Form 1)

NCD 047 368 642

V. INTAKE AND EFFLUENT CHARACTERISTICS (continued from page 3 of Form 2-C)

PART A - You must provide the results of at least one analysis for every pollutant in this table. Complete one table for each outfall. See instructions for additional details.

1. POLLUTANT	2. EFFLUENT							3. UNITS (specify if blank)	
	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS
	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
a. Biochemical Oxygen Demand (BOD)	71.0	675.9	26.8	207.1	5.8	37.8	465	mg/L	lb.
b. Chemical Oxygen Demand (COD)	32.1	313.2					1	mg/L	lb.
c. Total Organic Carbon (TOC)	84.9	828.4					1	mg/L	lb.
d. Total Suspended Solids (TSS)	44.0	387.8	22.0	177.0	9.8	54.6	465	mg/L	lb.
e. Ammonia (as N)	0.414	4.0					1	mg/L	lb.
f. Flow	VALUE 1.627		VALUE 1.133		VALUE 0.907		1095	MGD	MGD
g. Temperature (winter)	VALUE 26.0		VALUE 22.2		VALUE 18.4		118	°C	
h. Temperature (summer)	VALUE 32.0		VALUE 30.6		VALUE 29.0		118	°C	
i. pH	MINIMUM 6.37	MAXIMUM 8.47	MINIMUM n/a	MAXIMUM n/a			374	STANDARD UNITS	

PART B - Mark "X" in column 2-a for each pollutant you know or have reason to believe is present. Mark "X" in column 2-b for each pollutant you believe to be absent. If you mark column directly, or indirectly but expressly, in an effluent limitations guideline, you must provide the results of at least one analysis for that pollutant. For other pollutants for which quantitative data or an explanation of their presence in your discharge. Complete one table for each outfall. See the instructions for additional details and requirements.

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT							4. UNITS	
	a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
a. Bromide (24959-67-9)		X									
b. Chlorine, Total Residual	X		0.03	0.3					1	mg/L	lb.
c. Color	X		10	n/a					1	PCU	n/a
d. Fecal Coliform	X		est. 2	n/a					1	col/dL	n/a
e. Fluoride (16984-48-8)	X		170	1659					1	mg/L	lb.
f. Nitrate-Nitrite (as N)	X		0.065	0.6					1	mg/L	lb.

OUTFALL 001

ITEM V-B CONTINUED FROM FRONT

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT						4. UNITS		
	a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
g. Nitrogen, Total Organic (as N)	X		1.016	9.9					1	mg/L	lb.
h. Oil and Grease	X		<5.6	<50.0	5.2	42.5	0.26	1.87	36	mg/L	lb.
i. Phosphorus (as P), Total (7723-14-0)	X		12.4	121.0					1	mg/L	lb.
j. Radioactivity											
(1) Alpha, Total		X									
(2) Beta, Total		X									
(3) Radium, Total		X									
(4) Radium 226, Total		X									
k. Sulfate (as SO ₄) (14808-79-8)	X		1083	10568					1	mg/L	lb.
l. Sulfide (as S)		X									
m. Sulfite (as SO ₃) (14285-45-3)		X									
n. Surfactants	X		3.07	30.0					1	mg/L	lb.
o. Aluminum, Total (7429-90-5)	X		0.19	1.9					1	mg/L	lb.
p. Barium, Total (7440-39-3)		X									
q. Boron, Total (7440-42-8)		X									
r. Cobalt, Total (7440-48-4)		X									
s. Iron, Total (7439-89-6)	X		0.28	2.7					1	mg/L	lb.
t. Magnesium, Total (7439-95-4)	X		2.26	22.1					1	mg/L	lb.
u. Molybdenum, Total (7439-98-7)		X									
v. Manganese, Total (7439-96-5)	X		<0.005	<0.049					1	mg/L	lb.
w. Tin, Total (7440-31-5)		X									
x. Titanium, Total (7440-32-6)		X									

EPA I.D. NUMBER (copy from Item 1 of Form 1)

OUTFALL NUMBER

NCD 047 368 642

001

CONTINUED FROM PAGE 3 OF FORM 2-C

PART C - If you are a primary industry and this outfall contains process wastewater, refer to Table 2c-2 in the instructions to determine which of the GC/MS fractions you must test for fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2-a (secondary industries, nonprocess v fractions), mark "X" in column 2-b for each pollutant you know or have reason to believe is present. Mark "X" in column 2-c for each pollutant you believe is absent. If you provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for that pollutant if discharged in concentrations of 10 ppb or greater. If you mark column 2b for acrolein, acrylonitrile, 2,4 dinitrophenol, or 2-methyl-4, 6 dinitrophenol, you must provide the results of at least one analysis for that pollutant if discharged in concentrations of 100 ppb or greater. Otherwise, for pollutants for which you mark column 2b, you briefly describe the reasons the pollutant is expected to be discharged. Note that there are 7 pages to this part, please review each carefully. Complete one table (all 7 additional details and requirements).

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT						4. UNITS		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
METALS, CYANIDE, AND TOTAL PHENOLS												
1M. Antimony, Total (7440-36-0)	X			<0.002	<0.020					1	mg/L	lb.
2M. Arsenic, Total (7440-38-2)	X			<0.005	<0.049					1	mg/L	lb.
3M. Beryllium, Total (7440-41-7)	X			<0.001	<0.010					1	mg/L	lb.
4M. Cadmium, Total (7440-43-9)	X			<0.002	<0.020					1	mg/L	lb.
5M. Chromium, Total (7440-47-3)	X			0.010	0.070	0.010	0.070	0.004	0.034	4	mg/L	lb.
6M. Copper, Total (7440-50-8)	X			0.007	0.050	0.007	0.050	0.0055	0.047	4	mg/L	lb.
7M. Lead, Total (7439-92-1)	X			<0.003	<0.029					1	mg/L	lb.
8M. Mercury, Total (7439-97-6)	X			<0.0002	<0.002					1	mg/L	lb.
9M. Nickel, Total (7440-02-0)	X			0.012	0.090	0.012	0.090	0.0083	0.065	4	mg/L	lb.
10M. Selenium, Total (7782-49-2)	X			<0.005	<0.049					1	mg/L	lb.
11M. Silver, Total (7440-22-4)	X			<0.002	<0.020					1	mg/L	lb.
12M. Thallium, Total (7440-28-0)	X			<0.005	<0.049					1	mg/L	lb.
13M. Zinc, Total (7440-66-6)	X			0.042	0.390	0.042	0.390	0.0343	0.286	4	mg/L	lb.
14M. Cyanide, Total (57-12-5)	X			<0.005	<0.049					1	mg/L	lb.
15M. Phenols, Total	X			<0.0400	<0.390					1	mg/L	lb.
DIOXIN												
2,3,7,8-Tetra-chlorodibenzo-P-Dioxin (1784-01-8)			X	DESCRIBE RESULTS Not applicable								

OUTFALL 001

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3 EFFLUENT								4. UNITS	
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
GC/MS FRACTION – VOLATILE COMPOUNDS													
1V. Accrolein (107-02-8)	X			<0.0500	<0.488					1	mg/L	lb.	
2V. Acrylonitrile (107-13-1)	X			<0.0100	<0.098					1	mg/L	lb.	
3V. Benzene (71-43-2)	X			<0.00100	<0.10					1	mg/L	lb.	
4V. Bis (Chloromethyl) Ether (542-88-1)			X	Not Req	ired	per NCDWR	NPDES	Permitt'g	Unit				
5V. Bromoform (75-25-2)	X			<0.00100	<0.10					1	mg/L	lb.	
6V Carbon Tetrachloride (56-23-5)	X			<0.00100	<0.10					1	mg/L	lb.	
7V. Chlorobenzene (108-90-7)	X			<0.00100	<0.10					1	mg/L	lb.	
8V. Chlorodibromomethane (124-48-1)	X			<0.00100	<0.10					1	mg/L	lb.	
9V. Chloroethane (75-00-3)	X			<0.00500	<0.049					1	mg/L	lb.	
10V. 2-Chloroethylvinyl Ether (110-75-8)	X			<0.0500	<0.488					1	mg/L	lb.	
11V. Chloroform (67-66-3)	X			<0.00500	<0.049					1	mg/L	lb.	
12V. Dichlorobromomethane (75-27-4)	X			<0.00100	<0.10					1	mg/L	lb.	
13V. Dichlorodifluoromethane (75-71-8)	X			<0.00500	<0.049					1	mg/L	lb.	
14V. 1,1-Dichloroethane (75-34-3)	X			<0.00100	<0.10					1	mg/L	lb.	
15V. 1,2-Dichloroethane (107-06-2)	X			<0.00100	<0.10					1	mg/L	lb.	
16V. 1,1-Dichloroethylene (75-35-4)	X			<0.00100	<0.10					1	mg/L	lb.	
17V. 1,2-Dichloropropane (78-87-5)	X			<0.00100	<0.10					1	mg/L	lb.	
18V. 1,3-Dichloropropylene (542-75-6)	X			<0.00100	<0.10					1	mg/L	lb.	
19V. Ethylbenzene (100-41-4)	X			<0.00100	<0.10					1	mg/L	lb.	
20V. Methyl Bromide (74-83-9)	X			<0.00500	<0.049					1	mg/L	lb.	
21V. Methyl Chloride (74-87-3)	X			<0.00250	<0.024					1	mg/L	lb.	

CONTINUED FROM PAGE V-4

1 POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS	
	a. TESTING REQUIRED	b BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a CONCENTRATION	b MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
GC/MS FRACTION – VOLATILE COMPOUNDS (continued)													
22V. Methylene Chloride (75-09-2)	X			<0.00500	<0.049					1	mg/L	lb.	
23V. 1,1,2,2-Tetrachloroethane (79-34-5)	X			<0.00100	<0.010					1	mg/L	lb.	
24V. Tetrachloroethylene (127-18-4)	X			<0.00100	<0.010					1	mg/L	lb.	
25V. Toluene (108-88-3)	X			<0.00500	<0.049					1	mg/L	lb.	
26V. 1,2-Trans-Dichloroethylene (156-60-5)	X			<0.00100	<0.010					1	mg/L	lb.	
27V. 1,1,1-Trichloroethane (71-55-6)	X			<0.00100	<0.010					1	mg/L	lb.	
28V. 1,1,2-Trichloroethane (79-00-5)	X			<0.00100	<0.010					1	mg/L	lb.	
29V. Trichloroethylene (79-01-6)	X			<0.00100	<0.010					1	mg/L	lb.	
30V. Trichlorofluoromethane (75-69-4)	X			<0.00500	<0.049					1	mg/L	lb.	
31V. Vinyl Chloride (75-01-4)	X			<0.00100	<0.010					1	mg/L	lb.	
GC/MS FRACTION – ACID COMPOUNDS													
1A. 2-Chlorophenol (95-57-8)	X			<0.0100	<0.098					1	mg/L	lb.	
2A. 2,4-Dichlorophenol (120-83-2)	X			<0.0100	<0.098					1	mg/L	lb.	
3A. 2,4-Dimethylphenol (105-67-9)	X			<0.0100	<0.098					1	mg/L	lb.	
4A. 4,6-Dinitro-O-Cresol (534-52-1)	X			<0.0100	<0.098					1	mg/L	lb.	
5A. 2,4-Dinitrophenol (51-28-5)	X			<0.0100	<0.098					1	mg/L	lb.	
6A. 2-Nitrophenol (88-75-5)	X			<0.0100	<0.098					1	mg/L	lb.	
7A. 4-Nitrophenol (100-02-7)	X			<0.0100	<0.098					1	mg/L	lb.	
8A. P-Chloro-M-Cresol (59-50-7)	X			<0.0100	<0.098					1	mg/L	lb.	
9A. Pentachlorophenol (87-86-5)	X			<0.0100	<0.098					1	mg/L	lb.	
10A. Phenol (108-95-2)	X			<0.0100	<0.098					1	mg/L	lb.	
11A. 2,4,6-Trichlorophenol (88-05-2)	X			<0.0100	<0.098					1	mg/L	lb.	

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CONTINUED FROM THE FRONT

1 POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT							4. UNITS	
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS
				(1)	(2)	(1)	(2)	(1)	(2)			
				CONCENTRATION	MASS	CONCENTRATION	MASS	CONCENTRATION	MASS			
GC/MS FRACTION – BASE/NEUTRAL COMPOUNDS												
1B. Acenaphthene (83-32-9)	X			<0.00100	<0.01					1	mg/L	lb.
2B. Acenaphthylene (208-96-8)	X			<0.00100	<0.01					1	mg/L	lb.
3B. Anthracene (120-12-7)	X			<0.00100	<0.01					1	mg/L	lb.
4B. Benzidine (92-87-5)	X			<0.0100	<0.098					1	mg/L	lb.
5B. Benzo (a) Anthracene (56-55-3)	X			<0.00100	<0.01					1	mg/L	lb.
6B. Benzo (a) Pyrene (50-32-8)	X			<0.00100	<0.01					1	mg/L	lb.
7B. 3,4-Benzo-fluoranthene (205-99-2)	X			<0.00100	<0.01					1	mg/L	lb.
8B. Benzo (ghi) Perylene (191-24-2)	X			<0.00100	<0.01					1	mg/L	lb.
9B. Benzo (k) Fluoranthene (207-08-9)	X			<0.00100	<0.01					1	mg/L	lb.
10B. Bis (2-Chloro-ethoxy) Methane (111-91-1)	X			<0.0100	<0.098					1	mg/L	lb.
11B. Bis (2-Chloro-ethyl) Ether (111-44-4)	X			<0.0100	<0.098					1	mg/L	lb.
12B. Bis (2-Chloroisopropyl) Ether (102-80-1)	X			<0.0100	<0.098					1	mg/L	lb.
13B. Bis (2-Ethyl-hexyl) Phthalate (117-81-7)	X			<0.00300	<0.029					1	mg/L	lb.
14B. 4-Bromophenyl Phenyl Ether (101-55-3)	X			<0.0100	<0.098					1	mg/L	lb.
15B. Butyl Benzyl Phthalate (85-68-7)	X			<0.00300	<0.029					1	mg/L	lb.
16B. 2-Chloro-naphthalene (91-58-7)	X			<0.00100	<0.01					1	mg/L	lb.
17B. 4-Chloro-phenyl Phenyl Ether (7005-72-3)	X			<0.0100	<0.098					1	mg/L	lb.
18B. Chrysene (218-01-8)	X			<0.00100	<0.01					1	mg/L	lb.
19B. Dibenzo (a,h) Anthracene (53-70-3)	X			<0.00100	<0.01					1	mg/L	lb.
20B. 1,2-Dichloro-benzene (95-50-1)	X			<0.00100	<0.01					1	mg/L	lb.
21B. 1,3-Di-chloro-benzene (541-73-1)	X			<0.00100	<0.01					1	mg/L	lb.

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CONTINUED FROM PAGE V-6

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3 EFFLUENT						4. UNITS		
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCEN- TRATION	b. MAS:
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
GC/MS FRACTION – BASE/NEUTRAL COMPOUNDS (continued)												
22B. 1,4-Dichloro- benzene (106-46-7)	X			<0.00100	<0.001					1	mg/L	lb.
23B. 3,3-Dichloro- benzidine (91-94-1)	X			<0.0100	<0.098					1	mg/L	lb.
24B. Diethyl Phthalate (84-66-2)	X			<0.00300	<0.029					1	mg/L	lb.
25B. Dimethyl Phthalate (131 -11-3)	X			<0.00300	<0.029					1	mg/L	lb.
26B. Di-N-Butyl Phthalate (84-74-2)	X			<0.00300	<0.029					1	mg/L	lb.
27B. 2,4-Dinitro- toluene (121-14-2)	X			<0.0100	<0.098					1	mg/L	lb.
28B. 2,6-Dinitro- toluene (606-20-2)	X			<0.0100	<0.098					1	mg/L	lb.
29B. Di-N-Octyl Phthalate (117-84-0)	X			<0.00300	<0.029					1	mg/L	lb.
30B. 1,2-Diphenyl- hydrazine (as Azo- benzene) (122-66-7)	X			<0.0100	<0.098					1	mg/L	lb.
31B. Fluoranthene (206-44-0)	X			<0.00100	<0.001					1	mg/L	lb.
32B. Fluorene (86-73-7)	X			<0.00100	<0.001					1	mg/L	lb.
33B. Hexachloro- benzene (118-74-1)	X			<0.00100	<0.001					1	mg/L	lb.
34B. Hexachloro- butadiene (87-68-3)	X			<0.0100	<0.098					1	mg/L	lb.
35B. Hexachloro- cyclopentadiene (77-47-4)	X			<0.0100	<0.098					1	mg/L	lb.
36B Hexachloro- ethane (67-72-1)	X			<0.0100	<0.098					1	mg/L	lb.
37B. Indeno (1,2,3-cd) Pyrene (193-39-5)	X			<0.00100	<0.001					1	mg/L	lb.
38B Isophorone (78-59-1)	X			<0.0100	<0.098					1	mg/L	lb.
39B. Naphthalene (91-20-3)	X			<0.00100	<0.001					1	mg/L	lb.
40B. Nitrobenzene (98-95-3)	X			<0.0100	<0.098					1	mg/L	lb.
41B. N-Nitro- sodimethylamine (62-75-9)	X			<0.0100	<0.098					1	mg/L	lb.
42B. N-Nitrosodi- N-Propylamine (621-64-7)	X			<0.0100	<0.098					1	mg/L	lb.

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2 MARK "X"			3 EFFLUENT								4. UNITS	
	a TESTING REQUIRED	b BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
GC/MS FRACTION – BASE/NEUTRAL COMPOUNDS (continued)													
43B. N-Nitrosodiphenylamine (88-30-6)	X			<0.0100	<0.098					1	mg/L	1b.	
44B. Phenanthrene (85-01-8)	X			<0.00100	<0.001					1	mg/L	1b.	
45B. Pyrene (129-00-0)	X			<0.00100	<0.001					1	mg/L	1b.	
46B. 1,2,4-Trichlorobenzene (120-82-1)	X			<0.0100	<0.098					1	mg/L	1b.	
GC/MS FRACTION – PESTICIDES													
1P. Aldrin (309-00-2)	X			<0.000050	<5e-4					1	mg/L	1b.	
2P. α-BHC (319-84-8)	X			<0.000050	<5e-4					1	mg/L	1b.	
3P. β-BHC (319-85-7)	X			<0.000050	<5e-4					1	mg/L	1b.	
4P. γ-BHC (58-89-9)	X			<0.000050	<5e-4					1	mg/L	1b.	
5P. δ-BHC (319-88-8)	X			<0.000050	<5e-4					1	mg/L	1b.	
6P. Chlordane (57-74-9)	X			<0.000050	<0.005					1	mg/L	1b.	
7P. 4,4'-DDT (50-29-3)	X			<0.000050	<5e-4					1	mg/L	1b.	
8P. 4,4'-DDE (72-55-9)	X			<0.000050	<5e-4					1	mg/L	1b.	
9P. 4,4'-DDD (72-54-8)	X			<0.000050	<5e-4					1	mg/L	1b.	
10P. Dieldrin (60-57-1)	X			<0.000050	<5e-4					1	mg/L	1b.	
11P. α-Endosulfan (115-29-7)	X			<0.000050	<5e-4					1	mg/L	1b.	
12P. β-Endosulfan (115-29-7)	X			<0.000050	<5e-4					1	mg/L	1b.	
13P. Endosulfan Sulfate (1031-07-8)	X			<0.000050	<5e-4					1	mg/L	1b.	
14P. Endrin (72-20-8)	X			<0.000050	<5e-4					1	mg/L	1b.	
15P. Endrin Aldehyde (7421-83-4)	X			<0.000050	<5e-4					1	mg/L	1b.	
16P. Heptachlor (76-44-8)	X			<0.000050	<5e-4					1	mg/L	1b.	

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CONTINUED FROM PAGE V-8

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS	
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
GC/MS FRACTION – PESTICIDES (continued)													
17P. Heptachlor Epoxide (1024-57-3)	X			<0.000050	<5e-4					1	mg/L	lb.	
18P. PCB-1242 (53469-21-9)	X			<0.000500	<0.005					1	mg/L	lb.	
19P. PCB-1254 (11097-69-1)	X			<0.000500	<0.005					1	mg/L	lb.	
20P. PCB-1221 (11104-28-2)	X			<0.000500	<0.005					1	mg/L	lb.	
21P. PCB-1232 (11141-16-5)	X			<0.000500	<0.005					1	mg/L	lb.	
22P. PCB-1248 (12672-29-6)	X			<0.000500	<0.005					1	mg/L	lb.	
23P. PCB-1260 (11098-82-5)	X			<0.000500	<0.005					1	mg/L	lb.	
24P. PCB-1016 (12674-11-2)	X			<0.000500	<0.005					1	mg/L	lb.	
25P. Toxaphene (8001-35-2)	X			<0.000500	<0.005					1	mg/L	lb.	

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PLEASE PRINT OR TYPE IN THE UNSHADED AREAS ONLY. You may report some or all of this information on separate sheets (use the same format) instead of completing these pages.
SEE INSTRUCTIONS.

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V. INTAKE AND EFFLUENT CHARACTERISTICS (continued from page 3 of Form 2-C)

PART A – You must provide the results of at least one analysis for every pollutant in this table. Complete one table for each outfall. See instructions for additional details.

1. POLLUTANT	2. EFFLUENT							3. UNITS (specify if blank)	
	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO OF ANALYSES	a. CONCENTRATION	b. MASS
	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
a. Biochemical Oxygen Demand (BOD)	3.9	762.1	3.9	762.1	1.4	185.7	12	mg/L	lb.
b. Chemical Oxygen Demand (COD)	33.7	4898	33.7	4898	4.37	458.6	12	mg/L	lb.
c. Total Organic Carbon (TOC)	12.8	1135					1	mg/L	lb.
d. Total Suspended Solids (TSS)	10.6	939.7					1	mg/L	lb.
e. Ammonia (as N)	0.410	36.3					1	mg/L	lb.
f. Flow	VALUE 34.791		VALUE 26.813		VALUE 14.556		1095	MGD	MGD
g. Temperature (winter)	VALUE 22.0		VALUE 18.8		VALUE 14.1		188	°C	
h. Temperature (summer)	VALUE 33.0		VALUE 31.1		VALUE 30.0		190	°C	
i. pH	MINIMUM 6.11	MAXIMUM 8.16	MINIMUM n/a	MAXIMUM n/a			647	STANDARD UNITS	

PART B – Mark "X" in column 2-a for each pollutant you know or have reason to believe is present. Mark "X" in column 2-b for each pollutant you believe to be absent. If you mark column 2-a or 2-b, directly or indirectly but expressly, in an effluent limitations guideline, you must provide the results of at least one analysis for that pollutant. For other pollutants for which you do not provide quantitative data or an explanation of their presence in your discharge. Complete one table for each outfall. See the instructions for additional details and requirements.

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT							4. UNITS	
	a BELIEVED PRESENT	b BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS			
a. Bromide (24959-67-9)		X									
b. Chlorine, Total Residual	X		0.14	12.4					1	mg/L	lb.
c. Color	X		27	n/a					1	PCU	n/a
d. Fecal Coliform	X		est. 2	n/a					1	col/dL	n/a
e. Fluoride (16984-48-8)	X		35.1	4110	35.1	4110	17.3	1783	12	mg/L	lb.
f. Nitrate-Nitrite (as N)	X		2.4	442.9	2.4	442.9	1.04	127.5	36	mg/L	lb.

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ITEM V-B CONTINUED FROM FRONT

1. POLLUTANT AND CAS NO. (if available)	2. MARK "X"		3. EFFLUENT								4. UNITS	
	a. BELIEVED PRESENT	b. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
			(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
g. Nitrogen, Total Organic (as N)	X		0.362	32.1					1	mg/L	lb.	
h. Oil and Grease	X		<4.76	<422					1	mg/L	lb.	
i. Phosphorus (as P), Total (7723-14-0)	X		1.2	154	1.2	154	0.8	85.8	36	mg/L	lb.	
j. Radioactivity												
(1) Alpha, Total		X										
(2) Beta, Total		X										
(3) Radium, Total		X										
(4) Radium 226, Total		X										
k. Sulfate (as SO ₄) (14808-79-8)	X		105	9309					1	mg/L	lb.	
l. Sulfide (as S)		X										
m. Sulfite (as SO ₃) (14285-45-3)		X										
n. Surfactants	X		0.552	48.9					1	mg/L	lb.	
o. Aluminum, Total (7429-90-5)	X		1.27	112.6					1	mg/L	lb.	
p. Barium, Total (7440-39-3)		X										
q. Boron, Total (7440-42-8)		X										
r. Cobalt, Total (7440-48-4)		X										
s. Iron, Total (7439-89-6)	X		1.15	102.0					1	mg/L	lb.	
t. Magnesium, Total (7439-95-4)	X		2.26	200.4					1	mg/L	lb.	
u. Molybdenum, Total (7439-98-7)		X										
v. Manganese, Total (7439-96-5)	X		0.069	6.12					1	mg/L	lb.	
w. Tin, Total (7440-31-5)		X										
x. Titanium, Total (7440-32-6)		X										

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CONTINUED FROM PAGE 3 OF FORM 2-C

PART C - If you are a primary industry and this outfall contains process wastewater, refer to Table 2c-2 in the instructions to determine which of the GC/MS fractions you must test for fractions that apply to your industry and for ALL toxic metals, cyanides, and total phenols. If you are not required to mark column 2-a (secondary industries, nonprocess fractions), mark "X" in column 2-b for each pollutant you know or have reason to believe is present. Mark "X" in column 2-c for each pollutant you believe is absent. If you provide the results of at least one analysis for that pollutant. If you mark column 2b for any pollutant, you must provide the results of at least one analysis for that pollutant if discharged in concentrations of 10 ppb or greater. If you mark column 2b for acrolein, acrylonitrile, 2,4 dinitrophenol, or 2-methyl-4, 6 dinitrophenol, you must provide the results of at least one analysis for each of these pollutants which you know or have reason to believe that you discharge in concentrations of 100 ppb or greater. Otherwise, for pollutants for which you mark column 2b, you must briefly describe the reasons the pollutant is expected to be discharged. Note that there are 7 pages to this part, please review each carefully. Complete one table (all 7 additional details and requirements).

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS	
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
METALS, CYANIDE, AND TOTAL PHENOLS													
1M. Antimony, Total (7440-36-0)	X			<0.002	<0.177					1	mg/L	lb.	
2M. Arsenic, Total (7440-38-2)	X			<0.005	<0.443					1	mg/L	lb.	
3M. Beryllium, Total (7440-41-7)	X			<0.001	<0.089					1	mg/L	lb.	
4M. Cadmium, Total (7440-43-9)	X			<0.002	<0.177					1	mg/L	lb.	
5M. Chromium, Total (7440-47-3)	X			<0.005	<0.433					1	mg/L	lb.	
6M. Copper, Total (7440-50-8)	X			0.005	0.443					1	mg/L	lb.	
7M. Lead, Total (7439-92-1)	X			<0.003	<0.266					1	mg/L	lb.	
8M. Mercury, Total (7439-97-6)	X			<0.0002	<0.018					1	mg/L	lb.	
9M. Nickel, Total (7440-02-0)	X			<0.005	<0.433					1	mg/L	lb.	
10M. Selenium, Total (7782-49-2)	X			<0.005	<0.433					1	mg/L	lb.	
11M. Silver, Total (7440-22-4)	X			<0.002	<0.177					1	mg/L	lb.	
12M. Thallium, Total (7440-28-0)	X			<0.005	<0.433					1	mg/L	lb.	
13M. Zinc, Total (7440-66-6)	X			0.008	0.709					1	mg/L	lb.	
14M. Cyanide, Total (57-12-5)	X			<0.005	<0.433					1	mg/L	lb.	
15M. Phenols, Total	X			0.0433	3.84					1	mg/L	lb.	
DIOXIN													
2,3,7,8-Tetrachlorodibenzo-P-Dioxin (1764-01-6)			X	DESCRIBE RESULTS Not applicable									

OUTFALL 002

CONTINUED FROM THE FRONT

1 POLLUTANT AND CAS NUMBER (if available)	2 MARK "X"			3. EFFLUENT								4 UNITS	
	a TESTING REQUIRED	b BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
GC/MS FRACTION – VOLATILE COMPOUNDS													
1V. Accrolein (107-02-8)	X			<0.0500	<4.433					1	mg/L	lb.	
2V. Acrylonitrile (107-13-1)	X			<0.0100	<0.887					1	mg/L	lb.	
3V. Benzene (71-43-2)	X			<0.00100	<0.089					1	mg/L	lb.	
4V. Bis (Chloromethyl) Ether (542-88-1)			X	Not Req	ired	per NCDWR	NPDES	Permitt'g	Unit				
5V. Bromoform (75-25-2)	X			<0.00100	<0.089					1	mg/L	lb.	
6V. Carbon Tetrachloride (56-23-5)	X			<0.00100	<0.089					1	mg/L	lb.	
7V. Chlorobenzene (108-90-7)	X			<0.00100	<0.089					1	mg/L	lb.	
8V. Chlorodibromomethane (124-48-1)	X			<0.00100	<0.089					1	mg/L	lb.	
9V. Chloroethane (75-00-3)	X			<0.00500	<0.443					1	mg/L	lb.	
10V. 2-Chloroethylvinyl Ether (110-75-8)	X			<0.0500	<4.433					1	mg/L	lb.	
11V. Chloroform (67-68-3)	X			0.0248	2.199					1	mg/L	lb.	
12V. Dichlorodibromomethane (75-27-4)	X			0.00422	0.374					1	mg/L	lb.	
13V. Dichlorodifluoromethane (75-71-8)	X			<0.00500	<0.443					1	mg/L	lb.	
14V. 1,1-Dichloroethane (75-34-3)	X			<0.00100	<0.089					1	mg/L	lb.	
15V. 1,2-Dichloroethane (107-06-2)	X			<0.00100	<0.089					1	mg/L	lb.	
16V. 1,1-Dichloroethylene (75-35-4)	X			<0.00100	<0.089					1	mg/L	lb.	
17V. 1,2-Dichloropropane (78-87-5)	X			<0.00100	<0.089					1	mg/L	lb.	
18V. 1,3-Dichloropropylene (542-75-6)	X			<0.00100	<0.089					1	mg/L	lb.	
19V. Ethylbenzene (100-41-4)	X			<0.00100	<0.089					1	mg/L	lb.	
20V Methyl Bromide (74-83-9)	X			<0.00500	<0.443					1	mg/L	lb.	
21V. Methyl Chloride (74-87-3)	X			<0.00250	<0.222					1	mg/L	lb.	

CONTINUED FROM PAGE V-4

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS	
	a TESTING REQUIRED	b. BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCEN- TRATION	b. MAS	
				(1)	(2)	(1)	(2)	(1)	(2)				
				CONCENTRATION	MASS	CONCENTRATION	MASS	CONCENTRATION	MASS				
GC/MS FRACTION – VOLATILE COMPOUNDS (continued)													
22V. Methylene Chloride (75-09-2)	X			<0.00500	<0.443					1	mg/L	1b.	
23V. 1,1,2,2-Tetrachloroethane (79-34-5)	X			<0.00100	<0.089					1	mg/L	1b.	
24V. Tetrachloroethylene (127-18-4)	X			<0.00100	<0.089					1	mg/L	1b.	
25V. Toluene (108-88-3)	X			<0.00500	<0.443					1	mg/L	1b.	
26V. 1,2-Trans-Dichloroethylene (156-60-5)	X			<0.00100	<0.089					1	mg/L	1b.	
27V. 1,1,1-Trichloroethane (71-55-6)	X			<0.00100	<0.089					1	mg/L	1b.	
28V. 1,1,2-Trichloroethane (79-00-5)	X			<0.00100	<0.089					1	mg/L	1b.	
29V. Trichloroethylene (79-01-6)	X			<0.00100	<0.089					1	mg/L	1b.	
30V. Trichlorofluoromethane (75-69-4)	X			<0.00500	<0.443					1	mg/L	1b.	
31V. Vinyl Chloride (75-01-4)	X			<0.00100	<0.089					1	mg/L	1b.	
GC/MS FRACTION – ACID COMPOUNDS													
1A. 2-Chlorophenol (95-57-8)	X			<0.0100	<0.887					1	mg/L	1b.	
2A. 2,4-Dichlorophenol (120-83-2)	X			<0.0100	<0.887					1	mg/L	1b.	
3A. 2,4-Dimethylphenol (105-67-9)	X			<0.0100	<0.887					1	mg/L	1b.	
4A. 4,6-Dinitro-O-Cresol (534-52-1)	X			<0.0100	<0.887					1	mg/L	1b.	
5A. 2,4-Dinitrophenol (51-28-5)	X			<0.0100	<0.887					1	mg/L	1b.	
6A. 2-Nitrophenol (88-75-5)	X			<0.0100	<0.887					1	mg/L	1b.	
7A. 4-Nitrophenol (100-02-7)	X			<0.0100	<0.887					1	mg/L	1b.	
8A. P-Chloro-M-Cresol (59-50-7)	X			<0.0100	<0.887					1	mg/L	1b.	
9A. Pentachlorophenol (87-86-5)	X			<0.0100	<0.887					1	mg/L	1b.	
10A. Phenol (108-95-2)	X			<0.0100	<0.887					1	mg/L	1b.	
11A. 2,4,6-Trichlorophenol (88-05-2)	X			<0.0100	<0.887					1	mg/L	1b.	

OUTFALL 002

CONTINUED FROM THE FRONT

1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3. EFFLUENT								4. UNITS	
	a. TESTING REQUIRED	b. BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1)	(2)	(1)	(2)	(1)	(2)				
				CONCENTRATION	MASS	CONCENTRATION	MASS	CONCENTRATION	MASS				
GC/MS FRACTION – BASE/NEUTRAL COMPOUNDS													
1B. Acenaphthene (83-32-9)	X			<0.00100	<0.089					1	mg/L	1b.	
2B. Acenaphthylene (208-96-8)	X			<0.00100	<0.089					1	mg/L	1b.	
3B. Anthracene (120-12-7)	X			<0.00100	<0.089					1	mg/L	1b.	
4B. Benzidine (92-87-5)	X			<0.0100	<0.887					1	mg/L	1b.	
5B. Benzo (a) Anthracene (56-55-3)	X			<0.00100	<0.089					1	mg/L	1b.	
6B. Benzo (a) Pyrene (50-32-8)	X			<0.00100	<0.089					1	mg/L	1b.	
7B. 3,4-Benzo-fluoranthene (205-99-2)	X			<0.00100	<0.089					1	mg/L	1b.	
8B. Benzo (ghi) Perylene (191-24-2)	X			<0.00100	<0.089					1	mg/L	1b.	
9B. Benzo (k) Fluoranthene (207-08-9)	X			<0.00100	<0.089					1	mg/L	1b.	
10B. Bis (2-Chloroethoxy) Methane (111-91-1)	X			<0.0100	<0.887					1	mg/L	1b.	
11B. Bis (2-Chloroethoxy) Ether (111-44-4)	X			<0.0100	<0.887					1	mg/L	1b.	
12B. Bis (2-Chloroisopropyl) Ether (102-80-1)	X			<0.0100	<0.887					1	mg/L	1b.	
13B. Bis (2-Ethylhexyl) Phthalate (117-81-7)	X			<0.00300	<0.266					1	mg/L	1b.	
14B. 4-Bromophenyl Phenyl Ether (101-55-3)	X			<0.0100	<0.887					1	mg/L	1b.	
15B. Butyl Benzyl Phthalate (85-68-7)	X			<0.00300	<0.266					1	mg/L	1b.	
16B. 2-Chloronaphthalene (91-58-7)	X			<0.00100	<0.089					1	mg/L	1b.	
17B. 4-Chlorophenyl Phenyl Ether (7005-72-3)	X			<0.0100	<0.887					1	mg/L	1b.	
18B. Chrysene (218-01-9)	X			<0.00100	<0.089					1	mg/L	1b.	
19B. Dibenzo (a,h) Anthracene (53-70-3)	X			<0.00100	<0.089					1	mg/L	1b.	
20B. 1,2-Dichlorobenzene (95-50-1)	X			<0.00100	<0.089					1	mg/L	1b.	
21B. 1,3-Di-chlorobenzene (541-73-1)	X			<0.00100	<0.089					1	mg/L	1b.	

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1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3 EFFLUENT								4. UNITS	
	a TESTING REQUIRED	b BELIEVED PRESENT	c. BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d NO OF ANALYSES	a. CONCENTRATION	b. MAS	
				(1)	(2)	(1)	(2)	(1)	(2)				
				CONCENTRATION	MASS	CONCENTRATION	MASS	CONCENTRATION	MASS				
GC/MS FRACTION – BASE/NEUTRAL COMPOUNDS (continued)													
22B. 1,4-Dichlorobenzene (106-46-7)	X			<0.00100	<0.089					1	mg/L	1b.	
23B. 3,3-Dichlorobenzidine (91-94-1)	X			<0.0100	<0.887					1	mg/L	1b.	
24B. Diethyl Phthalate (84-66-2)	X			<0.00300	<0.226					1	mg/L	1b.	
25B. Dimethyl Phthalate (131-11-3)	X			<0.00300	<0.226					1	mg/L	1b.	
26B. Di-N-Butyl Phthalate (84-74-2)	X			<0.00300	<0.226					1	mg/L	1b.	
27B. 2,4-Dinitrotoluene (121-14-2)	X			<0.0100	<0.887					1	mg/L	1b.	
28B. 2,6-Dinitrotoluene (806-20-2)	X			<0.0100	<0.887					1	mg/L	1b.	
29B. Di-N-Octyl Phthalate (117-84-0)	X			<0.00300	<0.226					1	mg/L	1b.	
30B. 1,2-Diphenylhydrazine (as Azobenzene) (122-66-7)	X			<0.0100	<0.887					1	mg/L	1b.	
31B. Fluoranthene (206-44-0)	X			<0.00100	<0.089					1	mg/L	1b.	
32B. Fluorene (86-73-7)	X			<0.00100	<0.089					1	mg/L	1b.	
33B. Hexachlorobenzene (118-74-1)	X			<0.00100	<0.089					1	mg/L	1b.	
34B. Hexachlorobutadiene (87-68-3)	X			<0.0100	<0.887					1	mg/L	1b.	
35B. Hexachlorocyclopentadiene (77-47-4)	X			<0.0100	<0.887					1	mg/L	1b.	
36B. Hexachloroethane (67-72-1)	X			<0.0100	<0.887					1	mg/L	1b.	
37B. Indeno (1,2,3-cd) Pyrene (193-39-5)	X			<0.00100	<0.089					1	mg/L	1b.	
38B. Isophorone (78-59-1)	X			<0.0100	<0.887					1	mg/L	1b.	
39B. Naphthalene (91-20-3)	X			<0.00100	<0.089					1	mg/L	1b.	
40B. Nitrobenzene (98-95-3)	X			<0.0100	<0.887					1	mg/L	1b.	
41B. N-Nitrosodimethylamine (62-75-9)	X			<0.0100	<0.887					1	mg/L	1b.	
42B. N-Nitrosodi-N-Propylamine (621-64-7)	X			<0.0100	<0.887					1	mg/L	1b.	

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1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3 EFFLUENT								4. UNITS	
	a TESTING REQUIRED	b. BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO OF ANALYSES	a CONCENTRATION	b. MASS	
				(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS	(1) CONCENTRATION	(2) MASS				
GC/MS FRACTION – BASE/NEUTRAL COMPOUNDS (continued)													
43B. N-Nitro- sodiphenylamine (86-30-6)	X			<0.0100	<0.887					1	mg/L	lb.	
44B Phenanthrene (85-01-8)	X			<0.00100	<0.089					1	mg/L	lb.	
45B. Pyrene (129-00-0)	X			<0.00100	<0.089					1	mg/L	lb.	
46B. 1,2,4-Tri- chlorobenzene (120-82-1)	X			<0.0100	<0.887					1	mg/L	lb.	
GC/MS FRACTION – PESTICIDES													
1P. Aldrin (309-00-2)	X			<0.000050	<0.005					1	mg/L	lb.	
2P. α-BHC (319-84-6)	X			<0.000050	<0.005					1	mg/L	lb.	
3P. β-BHC (319-85-7)	X			<0.000050	<0.005					1	mg/L	lb.	
4P. γ-BHC (58-89-9)	X			<0.000050	<0.005					1	mg/L	lb.	
5P. δ-BHC (319-86-8)	X			<0.000050	<0.005					1	mg/L	lb.	
6P. Chlordane (57-74-9)	X			<0.000050	<0.044					1	mg/L	lb.	
7P. 4,4'-DDT (50-29-3)	X			<0.000050	<0.005					1	mg/L	lb.	
8P. 4,4'-DDE (72-55-9)	X			<0.000050	<0.005					1	mg/L	lb.	
9P. 4,4'-DDD (72-54-8)	X			<0.000050	<0.005					1	mg/L	lb.	
10P. Dieldrin (60-57-1)	X			<0.000050	<0.005					1	mg/L	lb.	
11P. α-Endosulfan (115-29-7)	X			<0.000050	<0.005					1	mg/L	lb.	
12P. β-Endosulfan (115-29-7)	X			<0.000050	<0.005					1	mg/L	lb.	
13P. Endosulfan Sulfate (1031-07-8)	X			<0.000050	<0.005					1	mg/L	lb.	
14P. Endrin (72-20-8)	X			<0.000050	<0.005					1	mg/L	lb.	
15P. Endrin Aldehyde (7421-93-4)	X			<0.000050	<0.005					1	mg/L	lb.	
16P. Heptachlor (76-44-8)	X			<0.000050	<0.005					1	mg/L	lb.	

EPA I.D. NUMBER (copy from Item 1 of Form 1)	OUTFALL NUMBER
NCD 047 368 642	002

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1. POLLUTANT AND CAS NUMBER (if available)	2. MARK "X"			3 EFFLUENT								4. UNITS	
	a. TESTING REQUIRED	b BELIEVED PRESENT	c BELIEVED ABSENT	a. MAXIMUM DAILY VALUE		b. MAXIMUM 30 DAY VALUE (if available)		c. LONG TERM AVRG. VALUE (if available)		d. NO. OF ANALYSES	a. CONCENTRATION	b. MASS	
				(1)	(2)	(1)	(2)	(1)	(2)				
				CONCENTRATION	MASS	CONCENTRATION	MASS	CONCENTRATION	MASS				
GC/MS FRACTION - PESTICIDES (continued)													
17P. Heptachlor Epoxide (1024-57-3)	X			<0.000050	<0.005					1	mg/L	lb.	
18P. PCB-1242 (53469-21-9)	X			<0.000500	<0.044					1	mg/L	lb.	
19P. PCB-1254 (11097-69-1)	X			<0.000500	<0.044					1	mg/L	lb.	
20P. PCB-1221 (11104-28-2)	X			<0.000500	<0.044					1	mg/L	lb.	
21P. PCB-1232 (11141-16-5)	X			<0.000500	<0.044					1	mg/L	lb.	
22P. PCB-1248 (12672-29-6)	X			<0.000500	<0.044					1	mg/L	lb.	
23P. PCB-1260 (11096-82-5)	X			<0.000500	<0.044					1	mg/L	lb.	
24P. PCB-1016 (12674-11-2)	X			<0.000500	<0.044					1	mg/L	lb.	
25P. Toxaphene (8001-35-2)	X			<0.000500	<0.044					1	mg/L	lb.	

Supplemental Information – Permit Renewal Application – April 27, 2016

Sludge Management Plan

The Chemours Company – Fayetteville Works operates a Class 3 Wastewater Treatment Plant which is comprised of a single-stage activated sludge biological system.

Excess sludge is removed from the system by diverting part of the Recycled Activated Sludge (at approximately 0.6% solids) from the clarifiers to a Dissolved Air Floatation (“DAF”) unit for initial thickening.

The sludge from the DAF (at approximately 3% solids) is transferred to a Mix Tank where polymer agents are added to enhance the dewatering process.

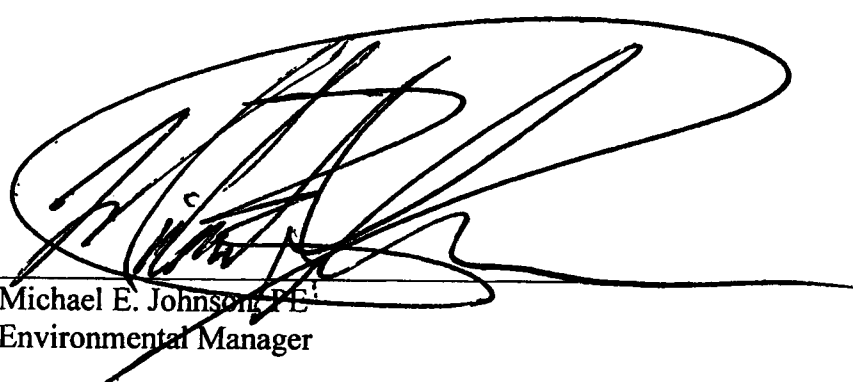
The semi-thickened sludge is transferred from the Mix Tank to a Rotary Filter for final thickening, whereby the sludge is thickened to 6% solids.

The thickened sludge is then transferred to a Screw Press where it is dewatered to a concentration of 9-20% solids.

Following the Screw Press, the sludge is typically dried in steam heated dryers to a concentration of 40-55% solids.

The dried sludge, or on occasion the dewatered sludge, is transported off-site to a commercial Subtitle D landfill. This sludge is currently being disposed of at the Waste Industries “Sampson County” Landfill near Roseboro, NC.

In 2015, the average weekly quantity of generated wasted sludge was approximately 35,000 lb.



Michael E. Johnson, PE
Environmental Manager

Supplemental Information – Permit Renewal Application – April 27, 2016**Current Facility Wastewater Management**

Process wastewater and stormwater from the various manufacturing areas are collected in the respective area sumps and ultimately conveyed via a gravity flow underground process sewer pipe to the facility's central wastewater treatment plant ("WWTP"). Sanitary sewage is conveyed via a separate underground sewer system to the WWTP. The permitted flowrate of the WWTP is 2.0 MGD, with an actual average flowrate of approximately 1.2 MGD.

This untreated process wastewater is commingled in the WWTP Influent Sump where it is pumped to an 850,000-gallon Equalization Basin. The Equalization Basin is mixed with two floating submerged mixers. Three floating surface aerators in the basin cool and aerate the incoming wastewater.

A 175,000-gallon Emergency Retention Tank is available for temporary storage of untreated wastewater which may need additional treatment or acclimation in the WWTP activated sludge process at a controlled rate that allows for proper biological treatment.

Untreated wastewater from the Equalization Basin is normally pumped to a 250,000-gallon Predigester Tank in which initial biological activity with the WWTP activated sludge begins. The Predigester Tank is aerated. The partially treated wastewater from the Predigester Tank is pumped to a 1,700,000-gallon Aeration Tank.

The Aeration Tank is the unit where the majority of the biological activity occurs. The Aeration Tank is aerated primarily by a diffused air system located in the bottom of the tank. The tank can have supplemental aeration via one or two floating Biomixers® that injects air through submerged rotors.

The biologically treated wastewater is then sent to one of two in-ground clarifiers (119,000 gallons and 168,000 gallons respectively) or an above-ground 679,000-gallon clarifier; with all clarifiers being operated in parallel. The clarified treated effluent is discharged to and through Outfall 001.

The wasted activated sludge is sent to a Dissolved Air Floatation (DAF) unit, then to a 47,000 gallon Sludge Storage Tank, and finally to a Rotary Filter for thickening. The thickened sludge is dewatered in a Sludge Press, and can be dried in a steam-heated dryer for additional moisture removal. The dewatered sludge or dewatered/dried sludge is transported off-site to a commercial Subtitle D landfill.

Non-contact process cooling water and non-process stormwater are conveyed via surface ditches. In addition, excess riverwater flow and Outfall 001 effluent are discharged directly to a surface ditch. The combined, total flow of water from the site is discharged through and monitored at Outfall 002. The discharged treated wastewater is conveyed via an underground pipe to the Cape Fear River, where it enters the river at a point approximately 1,500 feet upstream of the William O. Huske Lock & Dam (a.k.a Lock & Dam No. 3).

Supplemental Information – Permit Renewal Application – April 27, 2016**Current Facility Operating Conditions****Chemours Fluoromonomers/Nafion® Membrane Manufacturing Area:**

The Chemours Company – Fayetteville Works' Fluoromonomers / Nafion® Membrane manufacturing area produces several final products. Chemours™ Nafion® Membrane is a plastic film used in the chloroalkali industry and in electrochemical fuel cells. Chemours™ Nafion® Polymer Dispersions are used in the fabrication of thin films and coating formulations for fuel cells membranes, catalyst coatings, sensors, and a variety of electrochemical applications. The HFPO monomer and the Vinyl Ether monomers are used to manufacture various fluorochemical products such as Chemours™ Teflon®. Wastewater generated from this manufacturing facility is discharged to the Chemours' wastewater treatment plant.

Chemours Polymer Processing Aid ("PPA") Manufacturing Area:

The Chemours Company – Fayetteville Works' PPA manufacturing area produces a polymer processing aid. The processing aid produced in this unit is used in the manufacturing of fluoropolymers and fluorinated telomers, but none of the produced processing aid is used at the Fayetteville Works site. All process wastewater generated from this manufacturing facility is collected and shipped off-site for disposal. No process wastewater from this manufacturing facility is discharged to the Chemours' wastewater treatment plant or to the Cape Fear River.

Kuraray Butacite® Manufacturing Area:

The Kuraray America Inc. – Fayetteville Plant's Butacite® manufacturing area produces two final products. Kuraray™ Butacite® Interlayer plastic sheeting is the final product used in safety glass such as automobile windshields. Polyvinyl butyral resin is shipped off-site as a transfer to other Kuraray locations for final processing. Wastewater generated from this manufacturing facility is discharged to the Chemours' wastewater treatment plant.

Kuraray SentryGlas® Manufacturing Area:

The Kuraray America Inc. – Fayetteville Plant's SentryGlas® manufacturing area produces Kuraray™ SentryGlas® ionoplast interlayer laminate. SentryGlas® interlayer is used for laminated safety glass in side, rear, and overhead automobile windows. It is also used in architectural applications desiring safety glass. There is no contact process wastewater generated from this manufacturing facility, therefore only sanitary waste from this area is treated in the Chemours' wastewater treatment plant. This manufacturing facility does discharge non-contact cooling water to a surface ditch and ultimately to Outfall 002.

DuPont Polyvinyl Fluoride ("PVF") Manufacturing Area:

The DuPont Company – Fayetteville Works' PVF manufacturing area produces polyvinyl fluoride resin that is used in the electronics industry as a backing for photovoltaic cells, as well as many other uses. Wastewater generated from this manufacturing facility is discharged to the Chemours' wastewater treatment plant.

Supplemental Information – Permit Renewal Application – April 27, 2016**Alternate Application Schedule for §316(b) of the Clean Water Act**

Final regulations implementing §316(b) of the Clean Water Act, which establish requirements for cooling water intake structures at existing facilities, were published in the Federal Register on August 15, 2014 with an effective date of October 14, 2014.

The Chemours Company – Fayetteville Works (“Chemours”) operates a cooling water intake structure on the Cape Fear River that is subject to this new Federal Cooling Water Intake Structure Rule (“the Rule”) as codified in 40 CFR Part 125.

The Rule requires the owner or operator of a facility subject to Subpart J whose currently effective permit expires after July 14, 2018, to submit to the Director the information required in the applicable provisions of 40 CFR 122.21(r) when applying for a subsequent permit.

Pursuant to 40 CFR 125.95(a)(2), the owner or operator of a facility subject to Part 125 Subpart J, “Requirements Applicable to Cooling Water Intake Structures for Existing Facilities Under Section 316(b) of the Clean Water Act”, whose currently effective permit expires prior to July 14, 2018, may request the Director to establish an alternate schedule for the submission of the information required in 40 CFR 122.21(r) when applying for a subsequent (renewed) permit.

On October 20, 2015, a letter was sent from Michael E. Johnson, Environmental Manager, Chemours Company – Fayetteville Works, to Dr. Sergei Chernikov, NCDEQ Division of Water Resources’ NPDES Complex Permitting Unit, requesting an alternate schedule whereby all the materials required by the Rule will be submitted with the 2021 renewal application.

On February 26, 2016, a letter was sent from S. Jay Zimmerman, Director, NCDEQ Division of Water Resources, to Michael E. Johnson, Environmental Manager, Chemours Company – Fayetteville Works, wherein the requested alternate schedule for submission of required CWIS information with the next permit renewal in 2021 was approved. A copy of Mr. Zimmerman’s letter is attached to this application package.



PAT MCCRORY

Governor

DONALD R. VAN DER VAART

Secretary

S. JAY ZIMMERMAN

Director

February 26, 2016

Mr. Michael E. Johnson, P.E.
Environmental Manager
Chemours Company
22828 NC Highway 87 West
Fayetteville, North Carolina 28306-7332

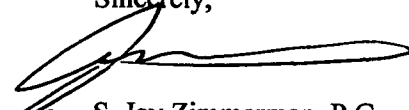
Subject: Alternate CWA 316(b) Application Schedule
NPDES Permit NC0003573
Fayetteville Works
Bladen County

Dear Mr. Johnson:

The Clean Water Act Section 316(b) Cooling Water Intake Structure (CWIS) Final Rule outlines regulations and standards for the design and operation of cooling water intake structures under the NPDES program. Your current permit expires October 31, 2016, with renewal application due by May 4, 2016. Since your permit expires prior to July 14, 2018, under 40 CFR 125.95(a)(2), you have requested an alternative schedule for submission of CWIS permit application information required in 40 CFR Part 122.21(r). Based on Division review, an alternate schedule for submission of required CWIS information with the next permit renewal in 2021 is approved. This schedule date will be established in the 2016 permit renewal as well.

Please note that facilities should begin to adapt their systems to comply with CWA Section 316(b) requirements. If you have any questions, please contact Tom Belnick with the NPDES Permitting Unit at 919-807-6390 or via email: tom.belnick@ncdenr.gov

Sincerely,


S. Jay Zimmerman, P.G.
Director, Division of Water Resources

Cc: NPDES File
Central File
Ec: US EPA Region 4
US FWS
NC WRC
NC DWR/Fayetteville Region

Supplemental Information – Permit Renewal Application – April 27, 2016**Elimination of Monitoring Requirement for PFOA**

In December 2002, the DuPont Company – Fayetteville Works began production of ammonium perfluorooctanoate (“APFO”), which is the ammonium salt of perfluorooctanoic acid (“PFOA”).

The renewed NPDES Permit No. NC0003573 that became effective on July 1, 2007, included a requirement for monthly monitoring of PFOA at Outfall 002.

In 2006 the North Carolina Division of Water Quality (“DWQ”), in consultation with the North Carolina Division of Waste Management and the North Carolina Department of Health and Human Services, established an Interim Maximum Allowable Concentration (“IMAC”) of 2 µg/L for PFOA, which was intended for the protection of groundwater as a source of drinking water.

Following the issuance of this temporary health-based level, DWQ requested the assistance of the North Carolina Secretary’s Science Advisory Board on Toxic Air Pollutants (“NCSAB”) in reviewing the toxicological literature on PFOA and recommending to DWQ an update of the IMAC for PFOA in groundwater. On August 10, 2012, the NCSAB issued their recommendation to DWQ that the IMAC for PFOA in groundwater be reduced to 1 µg/L.

During the 3-year period from 2013 to 2015, the average monthly concentration of the final effluent discharge at Outfall 002 was 0.027 µg/L PFOA, with a maximum concentration of 0.088 µg/L PFOA. During the same period, the average monthly concentration of the incoming water from the Cape Fear River to the site, which is 99% of the effluent flow at Outfall 002, was 0.012 µg/L PFOA, with a maximum concentration of 0.031 µg/L PFOA.

The production of APFO at this facility ceased in April 2013.

The Chemours Company – Fayetteville Works (formerly the DuPont Company – Fayetteville Works) is requesting that the monthly monitoring requirement for PFOA at Outfall 002 be eliminated in the renewed NPDES Permit No. NC0003573 for the following reasons:

- APFO is no longer manufactured at this facility and has not been produced at the facility since April 2013;
- APFO is not and has never been used as a process aid or a raw material at this facility;
- The 3-year average concentration at Outfall 002 was 0.027 µg/L PFOA, versus the current NC-DWR IMAC of 2 µg/L PFOA and the NCSAB recommended 1 µg/L PFOA; and
- PFOA is present at low concentrations throughout the Cape Fear River basin, and that background level of PFOA in the Cape Fear River water contributes to the concentration measured at Outfall 002.

Supplemental Information – Permit Renewal Application – April 27, 2016**Form 2C Permit Application – Bis(chloromethyl) ether**

Bis(chloromethyl) ether (CAS No. 542-88-1) was not analyzed for, and consequently was not reported on Page V-4 of Form 2C for both Outfall 001 and Outfall 002.

On November 28, 2014, the State of Oregon's Department of Environmental Quality ("ODEQ") issued a memorandum ^(Note 1) addressing the issue of analyzing for bis(chloromethyl) ether ("BCME"). In this memorandum, ODEQ states:

"Based on the chemical's rapid hydrolysis in water, there are no analytical methods to measure BCME in water samples. Currently, the only analytical techniques available for this compound are for air samples. Region 10 EPA staff queried its Manchester Environmental Lab in Port Orchard, WA about potential analytical methods for BCME. Staff at the lab confirmed that there is no EPA method for BCME because of its rapid degradation in water."

Because of the lack of an EPA approved analytical method for bis(chloromethyl) ether in a water matrix, ODEQ concluded:

"Given its rapid hydrolysis in water, there are no recommended analytical methods for BCME in water samples. Because BCME is not quantifiable in wastewater, DEQ will not require permit holders to monitor or conduct reasonable potential analyses for this toxic pollutant."

In an April 13, 2106, email from Tom Belnick, Supervisor of the NCDEQ Division of Water Resources' NPDES Complex Permitting Unit, to Michael Johnson, Environmental Manager, Chemours Company – Fayetteville Works, Mr. Belnick stated:

"I checked with our DWR analytical lab, and they concur with Oregon's position and are not aware of any labs using even R&D methods for this analyte. Therefore, you can omit this parameter from your application renewal."

Note 1: <http://www.deq.state.or.us/wq/standards/docs/toxics/BisChloromethylMemo.pdf>

Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)

Mark Strynar,^{*,†} Sonia Dagnino,^{†,‡} Rebecca McMahan,^{†,‡} Shuang Liang,^{†,‡} Andrew Lindstrom,[†] Erik Andersen,[†] Larry McMillan,[§] Michael Thurman,^{||} Imma Ferrer,^{||} and Carol Ball[⊥]

[†]National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States

[‡]Oak Ridge Institute for Science and Education, Oak Ridge, Tennessee 37831 United States

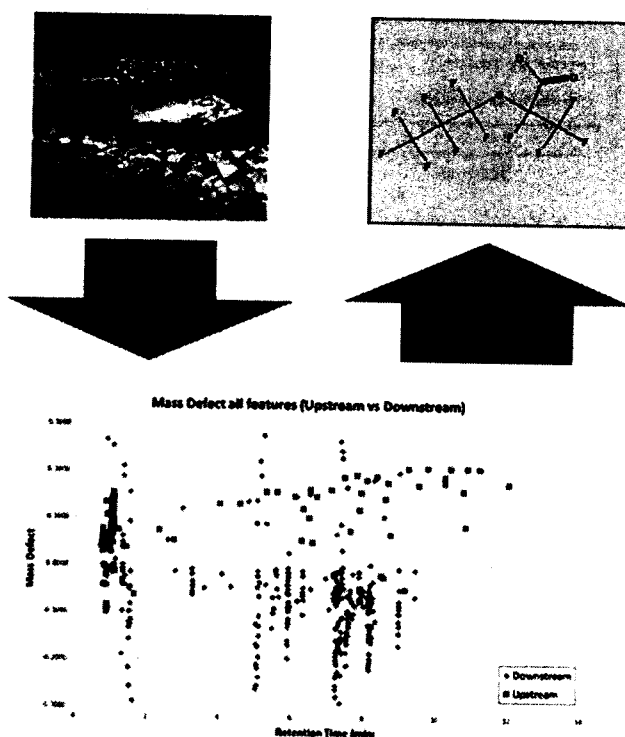
[§]National Caucus and Center on Black Aged, Inc., Durham, North Carolina 27713, United States

^{||}Center for Environmental Mass Spectrometry, University of Colorado Boulder, Boulder, Colorado 80309, United States

[⊥]Agilent Technologies Inc., Wilmington, Delaware 19808, United States

Supporting Information

ABSTRACT: Recent scientific scrutiny and concerns over exposure, toxicity, and risk have led to international regulatory efforts resulting in the reduction or elimination of certain perfluorinated compounds from various products and waste streams. Some manufacturers have started producing shorter chain per- and polyfluorinated compounds to try to reduce the potential for bioaccumulation in humans and wildlife. Some of these new compounds contain central ether oxygens or other minor modifications of traditional perfluorinated structures. At present, there has been very limited information published on these “replacement chemistries” in the peer-reviewed literature. In this study we used a time-of-flight mass spectrometry detector (LC-ESI-TOFMS) to identify fluorinated compounds in natural waters collected from locations with historical perfluorinated compound contamination. Our workflow for discovery of chemicals included sequential sampling of surface water for identification of potential sources, nontargeted TOFMS analysis, molecular feature extraction (MFE) of samples, and evaluation of features unique to the sample with source inputs. Specifically, compounds were tentatively identified by (1) accurate mass determination of parent and/or related adducts and fragments from in-source collision-induced dissociation (CID), (2) in-depth evaluation of in-source adducts formed during analysis, and (3) confirmation with authentic standards when available. We observed groups of compounds in homologous series that differed by multiples of CF_2 (m/z 49.9968) or CF_2O (m/z 65.9917). Compounds in each series were chromatographically separated and had comparable fragments and adducts produced during analysis. We detected 12 novel perfluoroalkyl ether carboxylic and sulfonic acids in surface water in North Carolina, USA using this approach. A key piece of evidence was the discovery of accurate mass in-source n -mer formation (H^+ and Na^+) differing by m/z 21.9819, corresponding to the mass difference between the protonated and sodiated dimers.



INTRODUCTION

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have unique physical and structural properties that make them extremely resistant to chemical and thermal degradation. As a result, PFASs have been used in a wide range of consumer

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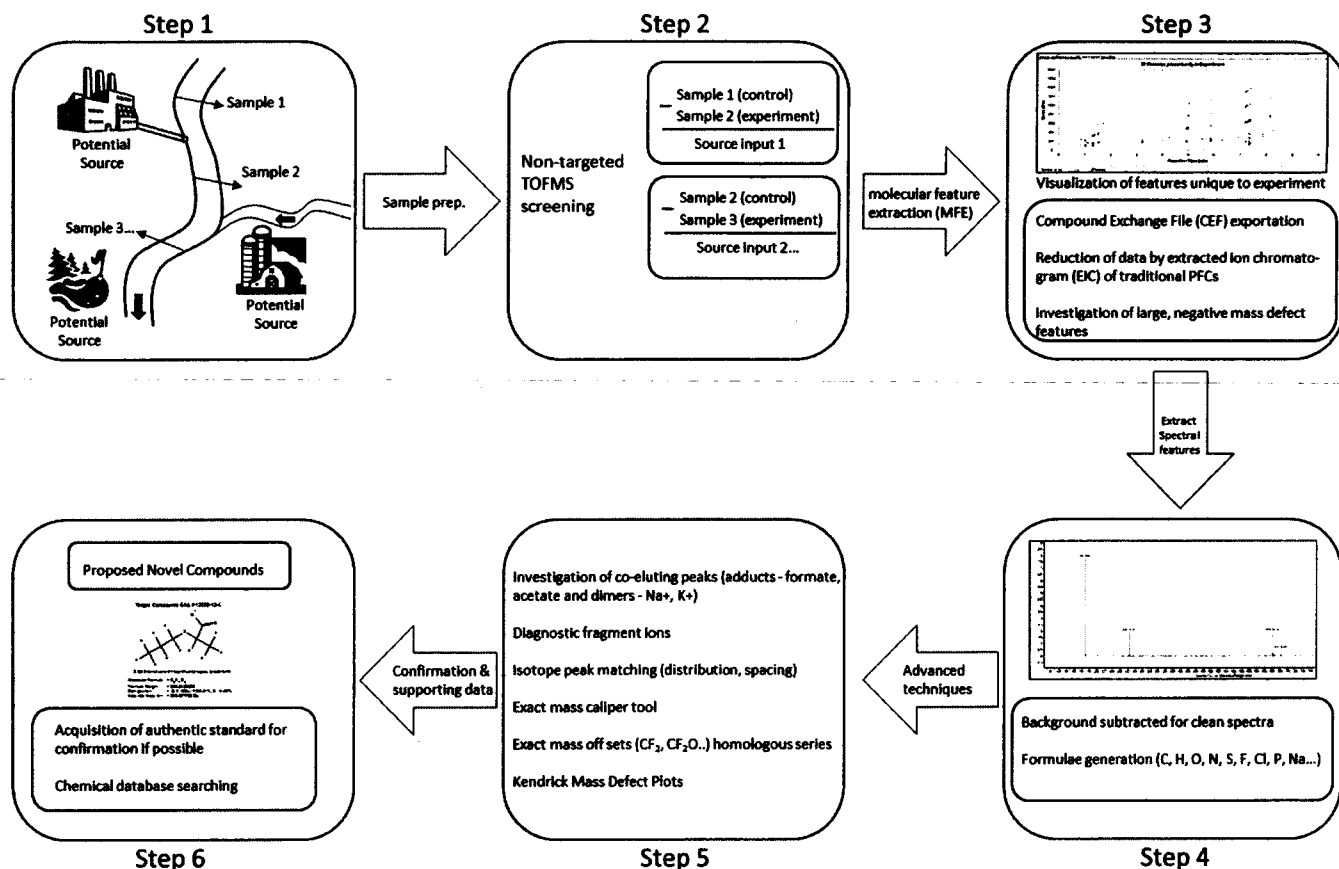


Figure 1. Sample workflow for TOFMS discovery.

products and industrial applications.¹ Between 1950 and 2000, the eight-carbon PFASs, including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), were among the most commonly produced and used perfluorinated compounds. PFASs have been detected in many environmental and biological matrices across the globe for a number of years,² and this ubiquity has led to mounting concerns about exposure and potential toxicity. As a result, many international regulatory efforts have been enacted to reduce, substitute, or eliminate long-chain (8 consecutive perfluorinated carbons or longer) PFASs from products and waste streams. In the United States, eight major fluorochemical manufacturers entered into a voluntary stewardship agreement with the U.S. Environmental Protection Agency (EPA) to phase out the use and production of long-chain perfluorinated chemistries by 2015.³ To take their place, manufacturers have started using alternative chemistries that may include both shorter-chain perfluorinated (<C8) and/or polyfluorinated materials. For example, some of these replacement compounds still have the traditional perfluorinated carbon regions, but they are broken into shorter units by insertion of ether oxygens at regular intervals. These ether linked compounds are still technically classified as perfluorinated if all carbons are substituted with fluorine and polyfluorinated if any carbon is occupied by a hydrogen rather than a fluorine.⁴ The rationale is that the addition of oxygens would likely make the replacement chemistry more labile to degradation, and thus more favorable for usage. However, to date the chemical manufacturers have disclosed little information publicly concerning the chemical structures and potential toxicities of the replacement PFASs now being produced. This makes it extremely difficult for independent

research groups to evaluate their environmental distributions and potential toxicities.

A rare exception is a peer-reviewed publication on 4,8-dioxo-3H-perfluorononanoate (ADONA) (Supporting Information Figure S1), a polyfluorinated alternative to PFOA which is said to have a "more favorable toxicological profile".⁵ This single journal article was published by its manufacturer, but standards for this new material have not been made available (to our knowledge) for comprehensive ecological or toxicological evaluation. Manufacturers typically submit more detailed information concerning compound structure, potential toxicity, environmental fate, and projected production volumes to regulatory authorities prior to large-scale production (e.g., the U.S. EPA's premanufacture notice process), but this information is held as confidential business information and cannot be disclosed to the general research community.

One example of industrial producers manufacturing replacement compounds is outlined in an executed draft consent order from the state of West Virginia to DuPont Corporation allowing the discharge of a new fluorinated compound into the Ohio river, at the Washington Works facility (West Virginia).⁶ This is the same facility that has been the source of historical PFOA contamination of local surface and groundwater due to industrial manufacture and discharge and is the center of a court-ordered investigation by the C8 science panel to determine if PFOA exposure in the local human population has led to adverse health effects.⁷ A number of recent epidemiological studies have indicated that exposure to PFOA at this location has been associated with adverse human health outcomes.^{8,9}

Typical environmental occurrence investigations have for years focused on targeted analysis for specific analytes of interest. Highly precise and sensitive LC and GC MS/MS methods have been developed to quantify contaminants of concern. A more recent approach for environmental sample analysis has been the use of high-resolution mass spectrometry (HRMS) for these efforts. Some researchers have used nontargeted or suspect screening effectively in demonstrating many chemical classes in wastewater effluent without the use of reference standards.^{11–13} These approaches have begun to rely more heavily on the use of databases, accurate mass searches, and HRMS molecular formula prediction capabilities for discovery. Confirmation with authentic standards still remains the “gold standard”. Schymanski et al.¹⁴ reported on five levels of confidence in identifying small molecules using HRMS ranging from exact mass matches, through molecular formula prediction, tentative candidate structures, library match searches, and finally confirmation with a reference standard. This is the type of approach that we use in this work to identify previously undescribed PFASs in surface water.

As it is mostly unknown what is being produced to replace traditional perfluorinated compounds, a series of sampling events was conducted to collect water samples with determination of new per- and polyfluorinated substances as a goal. In Nakayama et al.,¹⁰ a sampling of surface water in the Cape Fear River Basin in North Carolina indicated sources of perfluorinated compounds intermittently spread throughout the drainage basin. A follow-up investigation with more focused sampling to determine sources was not conducted. However, based on this early work, there was some indication that there were PFASs sources in the Fayetteville, NC area. More recent surface water sampling trips in this region indicated continued elevated concentrations of traditional perfluorinated compounds, supporting the Nakayama et al.¹⁰ findings. One such source was known to be downstream of the industrial effluent discharge of a fluorochemical production facility. Further investigation of these samples for identification and occurrence of potential replacement chemistries was undertaken.

MATERIALS AND METHODS

Sample Workflow for Discovery. A diagram of the workflow we used for novel compound discovery in surface water samples is shown in Figure 1. It is a six-step process that starts with sequential sampling of water, followed by nontargeted screening, visualization of detected peaks, further investigation of suspect features, advanced TOFMS techniques, and, last, compound confirmation with authentic standards when available. Using this approach, it becomes possible to detect chemicals that enter a waterway from a source (point or nonpoint) between sampling locations. This can then be used for such purposes as source elucidation, compound discovery, or both. In the following sections we will be referring to Figure 1 and the specific step in the process to which we are referring.

Sample Collection. In the summer of 2012, water samples were collected at locations on the Cape Fear River and its tributaries, with some locations having previously been found to contain measurable PFASs.¹⁵ Grab samples were taken from the bank and bridge crossings with a lab-made dip sampler or a stainless steel Kemmerer sampler, and stored in a 1-L HDPE bottle following the procedures described in Nakayama et al.¹⁶ Samples ($n = 9$) were acquired from the main flow of the Cape Fear River including from just south of the city of Fayetteville, NC to the bridge crossing in the town of Tar Heel, NC.

Duplicate samples, trip spikes, and trip blanks were included in this sampling. This sampling also included tributaries to the Cape Fear River along the same stretch of river where reclaimed wastewater treatment plant (WWTP) and industrial effluent streams occurred (Figure 1, step 1).

Sample Analysis for Traditional PFASs. Samples were prepared and analyzed according to the methods of Nakayama et al.¹⁶ In brief, water samples were stabilized with addition of nitric acid and stored at ambient temperature prior to analysis (<7 days). Each water sample was measured in a graduated cylinder, and the sampling bottle was washed with 10 mL of methanol to solubilize analytes that may have become sorbed to the container wall during shipping and storage. The water was then placed back in the methanol-washed bottle with the methanol rinsate, spiked with a mixture of internal standards, and filtered through a glass fiber filter. A volume, typically 500 mL, of water was concentrated on a Waters WAX SPE cartridge using a positive displacement pump. The cartridge was eluted with basic methanol (0.3% NH_4OH) and the eluent was concentrated via evaporation under N_2 gas to 1 mL and prepared for analysis. A procedural blank was prepared as described above using 500 mL of in-house DI water. Traditional PFASs (C_4 – C_{10} perfluorocarboxylic acids (PFCAs); perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), and PFOS) analysis was performed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (UPLC-MS/MS) (Waters, Milford, MA, USA).

TOFMS Investigation of Novel Fluorinated Compounds. The extraction method used for traditional PFASs analysis was also used for elucidation of novel compounds. Elevated concentrations of traditional PFASs in samples were used as an indication of samples that were likely closer to sources (Figure S2). Sample analysis was performed using an Agilent 1100 series HPLC interfaced with a 6210 series Accurate-Mass LC-TOF system (Agilent Technologies, Palo Alto, CA). The mass spectrometer was operated in electrospray ionization (ESI) negative mode and any drift in the mass accuracy of the TOF was continuously corrected by infusion of two reference compounds (purine (m/z 119.03632) and the acetate adduct of hexakis (1H,1H,3H-tetrafluoropropoxy) phosphazine (m/z 980.016375)) via dual-ESI sprayer. Chromatographic separation was accomplished using an Eclipse Plus C8 column (2.1 \times 50 mm, 3.5 μm ; Agilent). The method consisted of the following conditions: 0.2 mL/min flow rate; column at 30 $^\circ\text{C}$; mobile phases: A: ammonium formate buffer (0.4 mM) and DI water/methanol (95:5 v/v), and B: ammonium formate (0.4 mM) and methanol/DI water (95:5 v/v); gradient: 0–15 min a linear gradient from 75:25 A/B to 15:85 A/B; with a 4 min post time for equilibration.

Identification of Suspect Features. The total ion chromatogram (TIC) of each water sample was subjected to the software molecular feature extraction algorithm (MFE) and was restricted to the 100 most intense features m/z 50–1700 based on peak height. A molecular feature is defined as a single accurate mass with a specific retention time and an integrated area count. Compounds identified in the solvent and procedural blank samples were used to develop a mass exclusion list to subtract from subsequent unknown samples. After molecular features were identified, they were exported as a Compound Exchange File (.CEF) and imported into Mass Profiler to compare upstream with downstream samples.

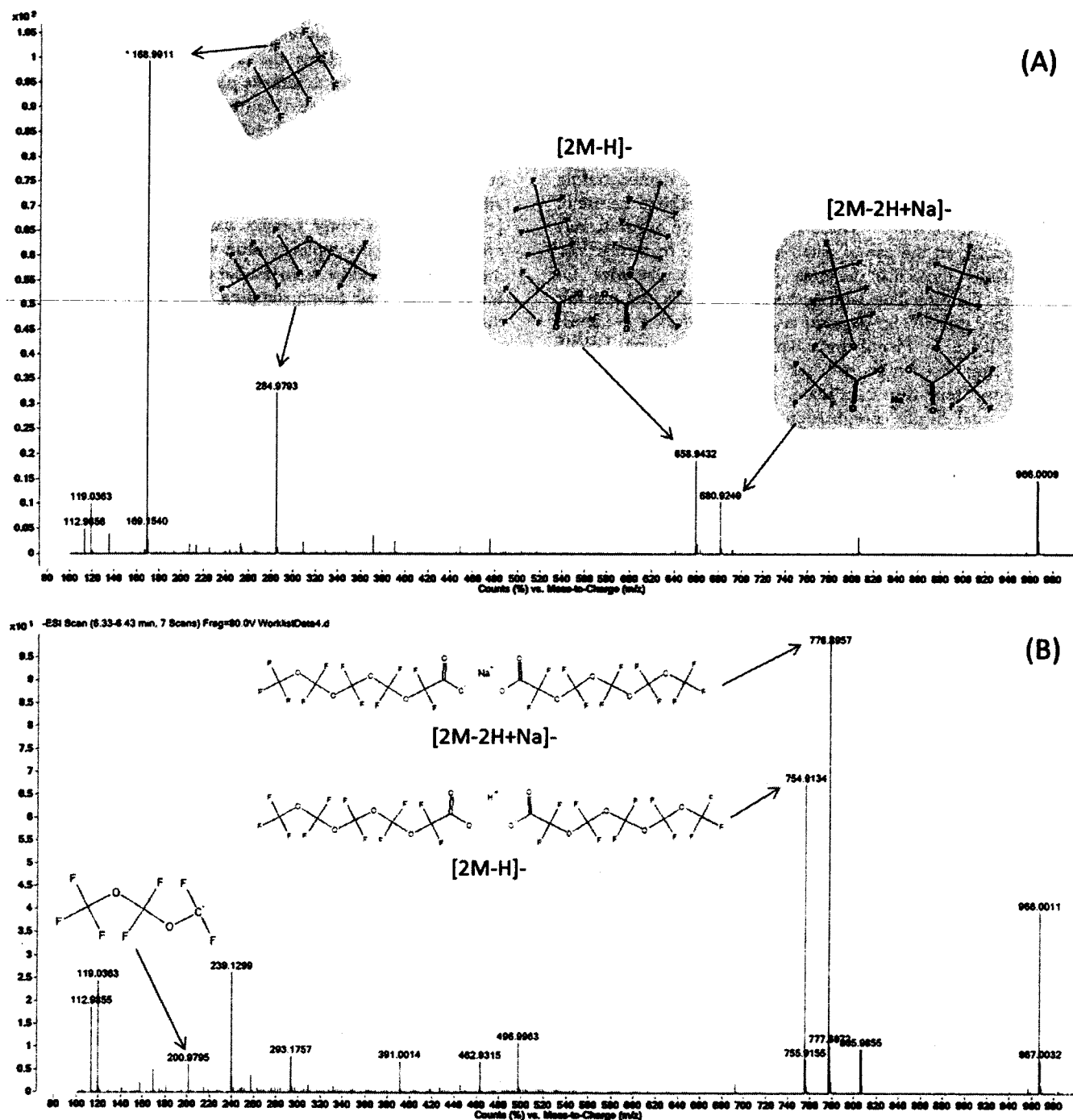


Figure 2. ESI negative spectra for two example perfluorinated ether carboxylic acids found in water: (A) $C_6HF_{11}O_3$ (retention time 5.9–6.0 min) and (B) $C_6HF_{11}O_6$ (retention time 6.5–6.6 min). Note: in spectrum (A and B) m/z 112.9856, 119.0363, and 966.0007 are reference masses for continuous mass calibration. Peaks not pointed out are not associated with the compound of interest.

Pairwise comparisons of sequential samples in river flow (Figure 1 step 2) were used to identify those requiring further investigation. For instance, features found in the downstream sample that were not found in the upstream sample indicate a source (point or nonpoint) exists between the two sampling locations (Figure 1 step 3). Further investigation of peaks with larger area counts using the “identify compounds” feature in the software and additional analyses of samples were used for confirmation. Perfluorinated compounds already identified with traditional UPLC-MS/MS analysis were eliminated from this

remaining list further narrowing the unknown compounds requiring follow-up scrutiny.

Poly- and perfluorinated compounds tend to have a negative mass defect due to the presence of multiple fluorine and oxygen atoms. Negative mass defect means that the exact mass of a compound is less than the nominal mass.¹⁷ For instance, the exact mass of perfluorooctanoate ($C_8F_{15}O_2$) is 412.9664, whereas the nominal mass is 413 Da. In this instance negative mass defect compounds only found in the downstream sample were further explored. An additional characteristic of samples that are contaminated with per- and polyfluorinated com-

Table 1. Accurate Mass of Polyfluorinated Compounds and In-Source Artifacts Found in Extracted Water Samples

number	formula	CAS no.	name	[M] ^a	[M - H] ⁻ m/z	[2M - 2H + Na] ⁻ m/z	[2M - H] ⁻ m/z
Monoether PFECAs							
1	C ₃ HF ₅ O ₃			179.9846	178.9773	380.9438	358.9619
2	C ₄ HF ₇ O ₃			229.9813	228.9740	480.9372	458.9553
3	C ₅ HF ₉ O ₃	863090-89-5		279.9782	278.9709	580.9310	558.9491
4	C ₆ HF ₁₁ O ₃	13252-13-6	undecafluoro-2-methyl-3-oxahexanoic acid	329.9750	328.9677	680.9247	658.9427
5	C ₇ HF ₁₃ O ₃			379.9718	378.9645	780.9182	758.9363
6	C ₈ HF ₁₅ O ₃			429.9686	428.9613	880.9118	858.9299
Polyether PFECAs							
7	C ₇ HF ₁₃ O ₇	39492-91-6	perfluoro-3,5,7,9,11-pentaoxadodecanoic acid	443.9515	442.9442	908.8776	886.8957
8	C ₆ HF ₁₁ O ₆	39492-90-5	perfluoro-3,5,7,9-butoxadecanoic acid	377.9598	376.9525	776.8942	754.9123
9	C ₅ HF ₉ O ₅	39492-89-2	perfluoro-3,5,7-propaoxaoctanoic acid	311.9681	310.9608	644.9108	622.9289
10	C ₄ HF ₇ O ₄	39492-88-1	perfluoro-3,5-dioxahexanoic acid	245.9764	244.9691	512.9274	490.9455
PFESAs							
11	C ₇ HF ₁₃ O ₅ S	66796-30-3 ^b		443.9337	442.9264		
12	C ₇ H ₂ F ₁₄ O ₅ S			463.9399	462.9326		
Other							
	Na ⁺			22.9892			
	H ⁺			1.0073			
	CF ₂ O			65.9917			
	CF ₂			49.9968			

^aIndicates the monoisotopic mass of the neutral species. ^bCAS number for Nafion copolymer.

pounds is the presence of multiple peaks that differ by exactly $\pm m/z$ 49.9968 and/or 65.9917, corresponding to a difference of CF₂ and CF₂O, respectively. This happens because PFAS synthesis is an industrial process that yields a distribution of products that differ primarily in chain length and/or degree of isomerization. Compounds identified as having a negative mass defect and differing from another peak by $\pm m/z$ 49.9968 and 65.9917 are highly likely to be polyfluorinated compounds. Selected samples were also analyzed by QTOF to aid with confirmation of proposed structures (generously provided by colleagues mentioned in the Acknowledgments).

TOFMS Experimental Workflow. Once an unknown compound with negative mass defect was noted, it was isolated from other mass spectral data in the following way: An extracted ion chromatogram (EIC) was generated from the total ion chromatogram (TIC) using the m/z identified. The EIC was then used to do a background subtraction of the spectral region both immediately before and after the detected peak (typically ± 0.1 min) (Figure 1 step 4). The center of the detected peak was extracted for the mass spectral information, and the background spectrum was subtracted for a clean spectrum. This was necessary to eliminate, to the best of our ability, competing spectral peaks that were coeluting and not associated with the spectrum being investigated. This would include, but is not limited to, spectral signals originating from the reference compounds (constantly infused to maintain a lock on mass assignments) and their fragments. Once suspect spectral signals were isolated, a series of experiments were conducted to induce in-source fragmentation ions to aid with compound identification based on the work of Ferrer and Thurman.¹⁸ Specifically, a series of methods with differing fragmentor voltages (80–190 V) were run in sequence to look for diagnostic ions that emerged as fragmentor voltage increased. In addition, common adducts such as Na⁺, NH₄⁺, acetate, etc. were used to aid with compound identification. Detected spectral features were subjected to molecular formula generation using the elements (C, H, O, N, S, P, Cl and F).¹⁹

Formulas generated were scored based on accurate mass, isotope abundance (compound mass distributions attributable to elemental mass distributions e.g., 1.1% ¹³C, 0.2% ¹⁸O, etc.) and isotope distribution (for example, slight differences in isotope mass such as when an $m+2$ peak is from two ¹³C or a single ¹⁸O). Only scores >75% were considered for further exploration. Figure 1 steps 4 and 5 outline the advanced TOFMS techniques used to discover novel chemical species.

RESULTS

With the approach described above, sites were identified for further investigation when a large increase in number and magnitude (area counts) of unknown compounds was found in downstream samples. In addition, a very large increase (greater than 2 orders of magnitude) in concentration of historically measured PFAAs also persisted for many river miles downstream of a certain point (Figure S2) consistent with observations in Nakayama et al.¹⁰ Interestingly, the profile of the historically measured PFASs contributing to the total PFASs found at each location was seen to dramatically change near this location (Figure S3). The major compounds contributing to this increase were perfluoropentanoic acid (PFPeA), followed by perfluoroheptanoic acid (PFHpA) and perfluorobutanoic acid (PFBA). It was evident that there was a significant source (total historically measured PFASs concentration increased by >100 times) of per- and polyfluorinated compounds near this location. Plotting the samples (CFR004 upstream vs CFR002 downstream) in MassProfiler for visualization indicated that there were 77 features that were unique to the downstream sample (Figure S4) with many ($n = 69$) having negative mass defects. In this figure (S4) the size of the symbol is proportional to the area counts of the molecular feature. Traditional PFASs with known concentrations (in Figure S2) are included for comparison purposes. Peaks with larger areas were investigated first under the assumption that these concentrations would be among the highest. Additional

pairwise comparisons were done on all sequential samples, however results indicated that samples downstream of CFR003 were simply dilutions of a source input. Samples were chosen for additional scrutiny where there was sufficient analytical signal without saturation of the detector which compromises mass accuracy.

Dimers and Fragments. It became evident that in multiple instances several of the larger peaks had a number of common characteristics: (1) negative mass defect, (2) multiple related chromatographic peaks differing by $\pm m/z$ 49.9968 and/or 65.9917 (\pm a CF_2 group and/or a CF_2O group), and (3) apparent noncovalent homodimers linked by either a proton or sodium ion. For example, at a retention time of 5.9–6.0 min, two large peaks emerged from the spectra with m/z of 658.9462 and 680.9256 (Figure 2A). After careful evaluation, it became apparent that these were the proton-bound and sodium-bound in-source homodimers of undecafluoro-2-methyl-3-oxahexanoic acid ($\text{C}_6\text{HF}_{11}\text{O}_3$) (Table 1). These differed by m/z 21.9819, the difference between the Na^+ and H^+ versions of the dimer. It is important to note that the $[\text{M} - \text{H}]^-$ peak (m/z 328.9677), which one might expect to be the most prominent, was barely distinguishable from the background signal at this point because the in-source ionization conditions so heavily favored the formation of these dimers. Given the prominence of the $\text{C}_6\text{HF}_{11}\text{O}_3$ compound in this sample, we postulated that a homologous series of related perfluorinated ether carboxylic acids (PFECAs), differing from the first compound by either the addition or deletion of CF_2 units (m/z 49.9968) might also be present. An EIC for each of the hypothetical masses, based on sequential addition or deletion of CF_2 units (m/z 49.9968) was extracted from the TIC, with the resulting series of related PFECAs presented in Figure S5. Although not specifically shown in this Figure, we also observed the presence of the analogous sodium and proton bound dimers for each compound identified in this homologous series of PFECAs ($\text{C}_{(n=3-8)}\text{HF}_{(n=5-15)}\text{O}_3$) (Table 1). To obtain additional evidence supporting the proposed structure of the compounds eluting at 5.9 min, additional experiments were conducted by altering the fragmentor voltage in order to try to form diagnostic ions from the m/z of 658.9427 and 680.9247 dimers eluting at this time. Figure S6 shows diagnostic dimer and fragment ions resulting from in-source CID that are consistent with the structure proposed for the $\text{C}_6\text{HF}_{11}\text{O}_3$ compound. The major ions found are also shown in Figure S10. Extracted spectra comparable to those shown in Figure S6, differing only by the loss of CF_2 groups, were investigated as well (Figure S7) lending credence to the postulated structure(s) and discussed in more detail in the following section.

Confirmation of Structure. An online search of the formula and proposed structure of the $\text{C}_6\text{HF}_{11}\text{O}_3$ compound eluting at 5.9 min led to a tentative match in a “grey-literature” citation that mentions a new-generation processing aid for the production of high-performance fluoropolymers identified only as C3 dimer acid/salt (CAS 13252-13-6) (Figure S6).⁶ With a CAS number, it was possible to purchase an authentic standard (Synquest Laboratories, Alachua, FL) to compare for retention times and mass spectral ionization patterns. The authentic standard compared very well with the tentatively identified compound found in water samples (± 0.051 min RT; $\pm m/z$ 0.0002 (0.51 ppm) (Figure 1 step 6). Additional authentic standards for other compounds in this homologous series were not commercially available. However, common spectral

patterns and adducts were observed differing only by repeating CF_2 units, as supporting information for compound identification of a homologous series of PFECAs (Figure S7).

Additional Perfluorinated Ether Acids. Figure S4 shows that there are a number of features that are present in the water sample downstream of a potential input location that are not in the upstream sample. Evident in Figure S4 are a pronounced series of peaks that appear as vertical lines, likely from coeluting and related chemicals (see later discussion on in-source n -mer formation). A number of these peaks exhibited negative mass defects. Further investigation of the TOFMS spectra indicated two peaks coeluting at 6.5 min (m/z 776.8942 and 754.9123) with a mass difference of m/z 21.9819, again suggesting the presence of in-source proton- and sodium-bound homodimers (Figure 2B). Knowing this information, we postulated an exact mass of m/z 376.9525 for the $[\text{M} - \text{H}]^-$ ion (Table 1). We further postulated a homologous series based on addition and deletion of CF_2 units, but exact masses corresponding to $\pm m/z$ 49.9968 were not detected. Given reports of industrial producers making greater use of ether oxygens to limit the size of perfluorinated regions within a given molecule, we postulated that a homologous series could also be based on the repeating units of CF_2O , with an exact mass offset of $\pm (m/z$ 65.9917).^{17,20} Searching the sample for m/z 376.9525 \pm this hypothetical CF_2O offset did yield another homologous series (Figure S8). In addition, as was previously the case, each of these new compounds was also found to form sodium-bound and proton-bound homodimers, providing further support for the proposed structures (Table 1). Confirmation of these compounds with authentic standards was not possible. It should be noted that in the homologous series shown, the chemical $\text{C}_3\text{HF}_5\text{O}_3$ (m/z 178.9773) is a common feature (Table 1) to the previously identified homologous series. Taken together, the exact mass of the proposed structures, the offset by a CF_2O , and the exact mass of the in-source dimers formed, all support the occurrence of this additional homologous series. One compound in this homologous series ($\text{C}_4\text{HF}_7\text{O}_4$ $[\text{M} - \text{H}]^-$ 244.9691 Table 1) was subjected to QTOF analysis leading to a series of accurate mass fragments consistent with the proposed structure (Figure S9). The accurate mass fragments show the sequential breakage of the ether oxygen bonds and the resulting fragment ions.

In-Source n -mer Formation. Multiple peaks originally thought to be of polymeric origin (m/z 1176.8353 and 1576.7769) were determined to be sodium-bound n -mers of m/z 376.9525 already identified (Figure S12). The retention time of these peaks (6.5 min) indicates this is an in-source phenomenon, as they coelute (Figure S4). In-source artifacts occur in the ESI source and can include such things as the formation of adducts (formate, Na^+ , H^+ , NH_4^+), fragments, dimers, trimers, and combinations of the above. Peaks that do not coelute, or are chromatographically separated, are generally considered not to be in-source artifacts. The observed spectra (Figure S12) include the formation of n -mers¹⁷ including 2 and 3 bound sodium cations in addition to the compounds shown in Figure S11. The formation of other n -mers with >1 bound sodium was seen as well for additional PFECAs found in this work (data not shown). Recent work by Trier et al.¹⁷ indicates that the formation of these polyfluorinated surfactant clusters occurs in the MS source in the gas phase and are pH and concentration dependent.¹⁷ However, this phenomenon may also be instrument-specific as sample dilution in this study did not lead to loss of these in-source dimers being formed. Similar

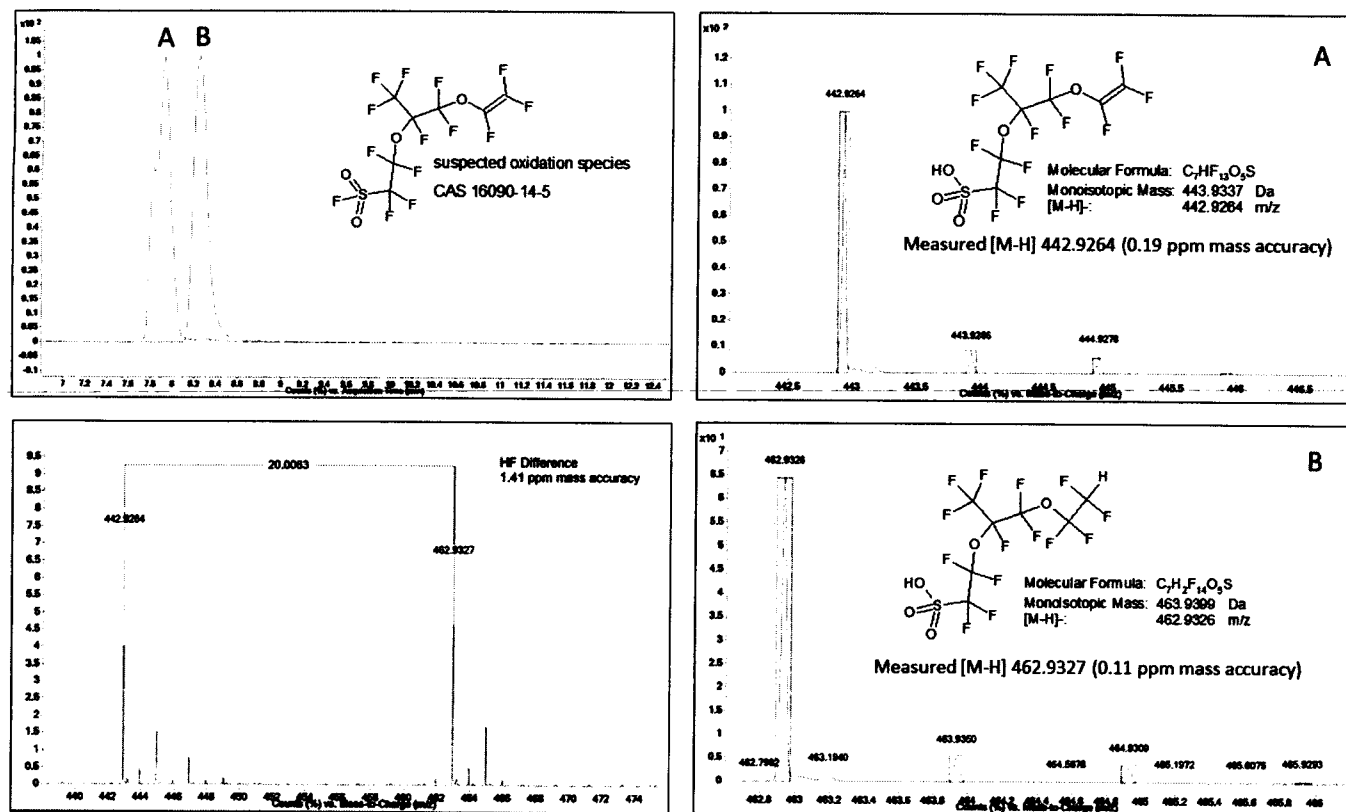


Figure 3. Suspected perfluoro ether sulfonic acids identified in water. Oxidation species are likely products of CAS 16090-14-5, a perfluorinated ether sulfonyl fluoride. Chromatogram shown of two resolved peaks (A,B) and isotope cluster matching of measured versus exact mass. Red boxes indicate the exact mass for the suspected formulas, compared to the accurate mass profile spectrum. Mass difference between two species is an HF (m/z 20.0063–1.41 ppm mass accuracy).

sodium- and proton-bound, as well as mobile phase, modifier (i.e., formate) adducts have been shown by Trier et al.¹⁷ for perfluorocarboxylic acids and mono-PAPs (perfluorinated alkyl phosphates).

Perfluoroalkyl Ether Sulfonic Acid (PFESA) Identification. Records of groundwater monitoring at a fluorochemical manufacturing plant with wells in close proximity to our sampling site indicate PFOA in $\mu\text{g/L}$ concentrations.²¹ This document also indicated a sulfonated tetrafluoroethylene based fluoropolymer-copolymer with the trade name Nafion was also produced at this facility. Our data provide evidence that materials related to this compound are also emitted into the river at this point. Figure 3 shows the chemical structures of the suspected oxidation species and resulting transformation products tentatively identified in our samples. An EIC of m/z 442.9264, which is the exact mass of the $[M - H]^-$ moiety of the copolymer containing the sulfonate group (IUPAC name 1,1,2,2-tetrafluoro-2-((1,1,1,2,3,3-hexafluoro-3-((trifluorovinyl)oxy)-2-propanyl)oxy)ethanesulfonic acid), suggests this compound is present in the water. In addition, spectral evidence supports the detection of a related compound which is consistent with the addition of an HF ($[M - H]^-$ m/z 462.9327) (IUPAC name 1,1,2,2-tetrafluoro-2-([1,1,1,2,3,3-hexafluoro-3-(1,1,2,2-tetrafluoroethoxy) propan-2-yl]oxy)ethanesulfonic acid). The two suspected compounds differ by the mass of HF (m/z 20.0062–1.41 ppm mass accuracy) (Figure 3). These compounds elute as two discrete chromatographic peaks, likely explained by the position occupied by the H and F additions. It is possible that these chemicals originate from the oxidation of ethanesulfonyl fluoride, 2-[1-(difluoro-

[(t(fluoroethenyl)oxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (CAS 16090-14-5) which may have been in use at this industrial location.²² These compounds would thus be classified as perfluoroalkyl ether sulfonic acids (PFESA).⁴ However, unlike previous perfluorinated ether carboxylic acid compounds found in this study, in-source proton- and sodium-bound dimers were not found for these perfluorinated ether sulfonates. In addition, a homologous series based on CF_2 or CF_2O additions was not found. We have not been able to obtain an authentic standard for confirmation of this proposed structure.

DISCUSSION

It has been well-known for a number of years that, due to the toxicity and persistence of perfluorinated compounds, industrial producers are moving toward shorter chain per- and polyfluorinated compound homologues. However, it is not well-known which compounds are being produced as replacements for historic perfluorinated compounds (e.g., PFOS and PFOA). Peer-reviewed literature showing the chemical structure of manufactured per- and polyfluorinated replacement compounds is sparse. An example of one such publication from 3M Corporation indicated that the compound ADONA (4,8-dioxo-3H-perfluorononanoate) is being made to replace ammonium perfluorooctanoate (APFO) as an emulsifier in the manufacture of fluoropolymers.⁵ The data presented in this study and Figure S1 indicate that the manufacture and release of per- and polyfluorinated compounds with CF_2 units interspersed with ether oxygen linkages likely is ongoing. A more recent study suggests that polyfluoroalkyl ether

compounds are being produced and that the number and spacing of ether oxygen linkages and size of the resulting per- and polyfluorinated compound may be manufacturer-specific including other major fluorochemical producers (DuPont, 3M, Solvay, and Asahi).²⁰ However, there are little to no data in the peer-reviewed literature on most of these compounds. The use of HRMS appears to be an ideal technique to use for discovery and occurrence of new PFASs being released into the environment.

As illustrated in this research, identification of previously undescribed compounds in environmental matrices can be made difficult by the formation of a multitude of in-source artifacts such as in-source gas phase adducts, *n*-mers, and the presence of a homologous series of per- and polyfluorinated compounds. D'Agostino and Mabury identified novel fluorinated surfactants in aqueous film-forming foams (AFFF) and commercial surfactant concentrates using high-resolution mass spectrometry.²³ Their results imply that there are a number of additional fluorinated compounds being produced and emitted into the environment that are unknown to most analysts. The use of TOFMS or other high-resolution mass spectrometers and the workflow we demonstrated (Figure 1) appears to be a useful way to determine occurrence and emissions of new and emerging fluorinated compounds for environmental occurrence efforts.

Schymanski et al. report on identifying small molecules via HRMS, with five levels of confidence.¹⁴ As has been noted earlier, one of the pitfalls of discovery work is the lack of authentic standards at times. As such the highest level of confidence for confirmed structure (Level 1) can be made to one compound in this effort, with the remaining compounds falling in the categories of tentative candidate(s) (Level 3) or probable structure (Level 2).¹⁴ An additional line of evidence we present that Schymanski et al. appear not to is the presence of a homologous series (CF₂, CF₂O) as evidence for compound identification.

The manufacture of shorter-chain perfluorinated and polyfluorinated compounds may have an advantageous effect on biological persistence and bioaccumulation. Two recent publications deemed "The Helsingor Statement"²⁴ and the "Madrid Statement"²⁵ explore the state of the science related to poly- and perfluorinated alkyl substances. Shorter straight-chain homologues of perfluorocarboxylic acids (<C₆) and sulfonic acids (<PFBS) have been shown to be cleared quickly from mammalian species tested and thus are not expected to bioaccumulate as readily as PFOS and PFOA.²⁶ However, the environmental persistence of these shorter chain perfluorinated compounds is likely to be no different from that of the related longer-chain acids. The conventional wisdom is the perfluorinated ether compounds will be more labile than the *n*-alkyl perfluorinated homologues with ether oxygen linkages being more susceptible to chemical or microbial attack. However, as the CF₂ bond in perfluorinated compounds is not at all open to microbial attack due to its bond strength, even the slightest degree of degradation of a per- or and polyfluorinated ether compound would be considered "more" labile. Environmental degradation or toxicology studies associated with the compounds identified in this study were not found by the authors in the peer-reviewed literature at the time of writing this Article. Although data are scarce, the few perfluoropolyethers (PFPEs) to have undergone any kind of degradation studies show little to no biodegradation or hydrolysis.²⁰ These data mainly come from the European Chemical Agency

(ECHA) database of registered substances and associated information.²⁷ Past studies have demonstrated poor removal efficiency for historical PFASs from source water to drinking water in conventional systems (i.e., treatments that do not include granular activated charcoal (GAC)). It is unknown if these PFECA and PFESA are removed by conventional WWTP processes.

Environmental Implications. We demonstrate the presence of a series of novel perfluorinated ether carboxylic and sulfonic acid(s) found to be in natural waters using a nontargeted workflow (Figure 1). The compounds consist of a homologous series of per- and polyfluorinated compounds with repeating units of CF₂ or CF₂O subunits. LC-TOFMS investigations of accurate mass dimers and *n*-mers (proton- or sodium-bound) in addition to diagnostic fragment ions support these findings. Further unidentified compounds with negative mass defects are likely also of per- and polyfluorinated origin, but have not yet been identified and are undergoing further analytical scrutiny. Nontargeted screening and discovery of novel species in samples such as reported here is an ongoing process. Additional environmental samples from other locations may be needed to identify additional chemistries.

Once a xenobiotic compound is identified in the environment, it falls upon the scientific community to begin monitoring efforts to find the extent of contamination of newly discovered species. In addition, toxicological and degradation investigations of identified compounds can commence once a compound has been identified. The procurement of authentic compounds for use in these types of investigations may be a major limiting factor in conducting such investigations, as most of these compounds appear not to be commercially available. More research will need to be conducted on these perfluorinated ether carboxylic and sulfonic acids concerning environmental occurrence, toxicology, and degradation potential.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01215.

Additional information including tables, figures, chemicals structures, and spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 919-541-3706; e-mail: strynar.mark@epa.gov.

Notes

The authors declare no competing financial interest.

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Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Nafion™

Ion Exchange Materials

Safety in Handling and Use

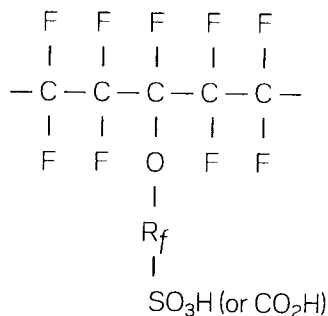
Technical Information

Introduction

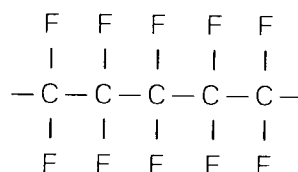
The purpose of this technical bulletin is to provide guidelines for the safe handling and use of Nafion™ perfluorinated membranes from Chemours. The complete contents should be reviewed before Nafion™ membranes are processed or used at elevated temperatures. For general background on fluoropolymer resins, reference can be made to the "Fluoropolymers Safe Handling Guide"—published by The Society of the Plastics Industry.

Nafion™ perfluorinated membranes are fabricated from copolymers of tetrafluoroethylene and perfluorinated monomers containing sulfonic acid end groups or from copolymers containing both sulfonic acid and carboxylic acid groups. The safety considerations for these membranes are based on the thermal and combustion decomposition products of the copolymers.

The perfluorinated membranes are composed of carbon-fluorine backbone chains with perfluoro side chains containing sulfonic acid groups. The chemical structure is shown below:



The analogous structure for Teflon™ PTFE fluoropolymer resins is:



The Nafion™ perfluorinated membranes have the extraordinary chemical and thermal stability of Teflon™ resins. While Teflon™ resin is one of the most hydrophobic substances known, Nafion™ membranes are one of the most hydrophilic. They absorb water and some polar organics rapidly, even at room temperature, in amounts dependent upon the number of sulfonic and carboxylic groups. Whereas Teflon™ resin is chemically inert, the Nafion™ membranes are strong polymeric acids, which react with organic and inorganic bases. However, the sulfonic and carboxylic acid groups in the polymer are essentially immobile and immersed in a fluoropolymer matrix. Consequently, membranes can contact the skin without producing irritation.

Since the development of perfluorinated membranes, several thousand kilograms have been used in many applications. During this time, there have been no reported cases of injury resulting from handling or exposure to these products.

Ingestion

The perfluorinated sulfonic acid copolymers used in Nafion™ membranes exhibit very low acute toxicity when administered in oral doses to rats. The LD50s are greater than 20,000 mg/kg of body weight.

Skin Contact

When tested on rabbits, perfluorinated sulfonic acid copolymers used in Nafion™ membranes were not irritating to the skin. Tests designed to determine the skin irritation and sensitization potential of these materials was also conducted with human volunteers. The results indicated that no unusual dermatitis hazard could be expected in the normal use of membranes for non-apparel industrial applications. Prolonged contact, however, may be irritating to the skin of certain individuals.

Nafion™ at High Temperatures

Almost without exception, the fumes from decomposing materials, such as Nafion™, Teflon™, and other plastics in high-temperature environments are objectionable from the standpoint of health and safety. However, Nafion™ and other fluoropolymers are more resistant to decomposition at higher temperatures than most other thermoplastics.

The maximum continuous operating temperature of Nafion™ perfluorinated sulfonic acid copolymer is about 175 °C (347 °F) in anhydrous systems. In aqueous and organic systems with proton-donating solvents, the maximum temperature is higher; for example, stability in aqueous systems at 220–240 °C (428–464 °F) has been demonstrated for several days.

The perfluorinated carboxylic acid copolymer, as used in the Nafion™ 900/2000 series, is less resistant to elevated temperatures; however, Nafion™ membranes containing perfluorinated carboxylic acid copolymer are intended primarily for use below 120 °C (248 °F).

Fumes should present no problems, except during heat sealing operations.

Polymer Fume Fever

Exposure to thermal decomposition products of Nafion™ perfluorinated membranes may cause a temporary flu-like condition. The symptoms do not ordinarily occur until several hours after exposure, and pass within 24 to 48 hours, even in the absence of treatment. Observations indicate that for other fluoropolymer resins these attacks have no lasting effect, and the effects are not cumulative. These attacks would be expected to occur after exposure to vapors evolved from the polymer at temperatures above 250 °C (482 °F) or from smoking cigarettes and/or tobacco contaminated with the polymer.

Thermal Degradation Products

Using a standard Infrared Analysis of Thermal Effluents (IRATE) technique, the composition of the effluent from perfluorinated sulfonic acid copolymer was determined at the following conditions: the atmosphere was air, flow rate 13 mL/min, sample size 0.5 g. The sample heated in a stainless steel tube at 10 °C (18 °F)/min to 200 °C (392 °F), and then 5 °C (9 °F)/min to 400 °C (752 °F) and held for an additional 20 min, giving a total run time of about 75 min. The results are shown below:

Degradation Products of Sulfonic Acid Copolymer

Compound	Evolution Temperature (°C)	Mass Percent
SO ₂	280 (536)	15
CO ₂	300 (572)	30
HF	400 (752)	*
CO	400 (752)	3
R _f COF	400 (752)	10**
COF ₂	400 (752)	3
COS	400 (752)	Trace
R _f OH	400 (752)	Trace

*Significant level, but could not calculate because HF reacts with and absorbs on cell walls.

**Mixture of products.

Repetitive IR scans of the effluent gave the approximate evolution temperature for each product, while amounts were determined by collecting air in a 1-meter IR cell and examining its spectrum. The perfluorinated carboxylic copolymer used in the Nafion™ 900/2000 series was studied by IRATE using an atmosphere of nitrogen and heating from 250–450 °C (482–842 °F) at 5 °C (9 °F)/min. Decomposition began at approximately 320 °C (608 °F) and yielded mainly CO₂ plus some CO, tetrafluoroethylene, hexafluoropropylene, and hydrogen fluoride. Stability is reduced, however, in air. Differential thermal analysis detects decomposition in air at 150 °C (302 °F), yielding a product identified by mass spectroscopy as CO₂ (decarboxylation).

Ventilation Recommendations When Heating Nafion™ Perfluorinated Membranes

Nafion™ perfluorinated membranes are not suitable for melt processing. Thermal decomposition begins before the membranes become fluid enough for shaping. However, at times, it is desirable to heat seal films and laminates to form tubes, pockets, etc. In heat sealing, temperatures in the range of 300 °C (572 °F) are

encountered for brief intervals, and only a small amount of material is exposed to the decomposition temperature.

When Nafion™ perfluorinated membranes are exposed or used at elevated temperatures, good safety practice requires the use of adequate ventilation to prevent inhalation of irritating, toxic fumes and gases that may evolve. Normal ventilation required for personnel in work areas may not be sufficient for all operations. Therefore, it is recommended that a local exhaust ventilation system, in addition to normal ventilation, be used whenever

Nafion™ is heated above 150 °C (302 °F) in the work area. Strict adherence to this practice will prevent discomfort or injury to personnel.

Flammability

Nafion™ perfluorinated membranes will not burn in air, but will burn in environments that are highly oxygen-enriched. The limiting oxygen index (LOI), as measured by the "candle test" (ASTM D2863-77), is 95%.

As a fuel, Nafion™ perfluorinated membranes have a comparatively low rating. Heat of combustion is about 5.8 MJ/kg (2,500 Btu/lb) compared to 46 MJ/kg (20,000 Btu/lb) for polyethylene.

Questions may arise concerning fire hazards associated with the storage of Nafion™ perfluorinated membranes. In essentially all situations, whether in storage or use, the quantity of Nafion™ material involved is so small in proportion to other materials that its presence is unlikely to add appreciably to other hazards attendant to a fire. Bulk quantities (over 50 kg) should be stored away from flammable materials.

In the event of fire, temperatures may rise above the decomposition temperature of Nafion™; thus, liberating hydrogen fluoride and other volatile fluoropolymers. Under these conditions, personnel entering the storage or use area should wear self-contained breathing apparatus and full protective equipment to minimize contact with the skin. This type of equipment is standard in fighting many types of fires. All types of chemical extinguishers may be used to fight fires involving Nafion™. Large quantities of water may also be used to cool and extinguish the fire.

Waste Disposal

The preferred method of waste disposal of Nafion™ perfluorinated products is landfill in compliance with government regulations. Nafion™ materials are not biodegradable, contain no extractable material, and are unaffected by exposure to sunlight, seawater, or fresh water. An alternative method is incineration. Small quantities of Nafion™ materials, up to 10 lb at a time, can be incinerated along with general plant refuse, if special precautions are followed. Incineration of Nafion™ materials above 800 °C (1472 °F) in the presence of normal organic refuse produces sulfur dioxide, hydrogen fluoride, and carbon dioxide. Hydrogen fluoride causes eye and nose irritation before approaching systemic toxic levels, and may also affect certain vegetation. Therefore, to reduce hydrogen fluoride concentration to an acceptable amount (less than 1 part per billion at ground level), the incinerator should have alkaline scrubbing facilities.

The data listed here fall within the normal range of product properties, but they should not be used to establish specification limits nor used alone as the basis of design. This information is based on technical data that Chemours believes to be reliable. It is intended for use by persons having technical skill and at their own discretion and risk. This information is given with the understanding that those using it will satisfy themselves that their particular conditions of use present no health or safety hazards. Because conditions of product use are outside our control, Chemours makes no warranties, express or implied, and assumes no obligation or liability in connection with any use of this information or for results obtained in reliance thereon. The disclosure of the information is not a license to operate under or a recommendation to infringe any patent of Chemours or others.

Medical Statement: Please contact your Chemours representative to discuss limitations regarding medical applications.

For more information about Nafion™, contact:

The Chemours Company FC, LLC

Global Customer Service for IXM

22828 NC Highway 87 W

Fayetteville, NC 28306, U.S.A.

Telephone U.S.A.: (800) 283-2493

Fax: (302) 861-3736

Email: customerservice.nafion@chemours.com

Web: chemours.com/Nafion

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C-10601 (1/16)

Adams, Jennifer H

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Tuesday, June 20, 2017 2:06 PM
To: Adams, Jennifer H
Subject: Re: CFPUA Investigation of Study Timeline
Attachments: PFECAs_Sun_ESTL2016.pdf; Ethers_Strynar_EST2015.pdf

Hi Jennifer,

I am at a conference in Michigan right now. I can call you around 4:30 pm.

In response to your questions:

1. The genesis of the initial study (2013-2014 samples) was the interest of my research group and my EPA collaborators to learn which compound replaced PFOA, the polymer processing aid DuPont/Chemours had been making at the Fayetteville Works. No one requested the study. Based on my recollection (I would have to verify exact dates), my EPA colleagues first identified GenX as the PFOA replacement in 2012. In 2013, we were able to obtain an analytical standard for GenX and began measuring GenX in the samples collected in 2013. At that time, the identity of the other ethers we describe in the attached 2016 ES&T Letters paper (Sun et al.) had not yet been identified.
2. The 2015 research proposal, which was funded by NSF built on the 2013/4 results. The objectives of the 2015 study are to provide concentration estimates for the ethers other than GenX (we published only peak area counts in our 2016 paper by Sun et al. for the other ethers) and to trace the concentrations of GenX and other ethers from the Chemours plant to the Kings Bluff intake and through CFPUA's distribution system. We are still conducting this study.
3. The method for the other ethers was developed in 2014. The identity of the other ethers was first published in 2015 in the attached ES&T paper (Strynar et al.). In 2014, we collected additional samples from the Cape Fear River and in the Sweeney WTP that we analyzed within a week for GenX and the other ethers (Figure 2 in the ES&T Letters paper by Sun et al.).

I am happy to answer more questions when we connect by phone ~4:30 pm.

Best,

Detlef

On 6/20/17 12:27 PM, Adams, Jennifer H wrote:

Afternoon Dr. Knappe – I left you a voice mail earlier – I'm on the Board of Directors of the Cape Fear Public Utility Authority, and have been tasked with understanding the timeline of the entire study. What I would like to discuss with you is the following:

- What was the genesis of the initial study? Was it an EPA request?
- From what I've determined, the study was proposed in 2015, and then published in 2016. The study included development of an analytical method for PFECA. However, samples used in the study were taken from the CFPUA raw water intake in 2013. How could samples be analyzed for

a method that had not yet been developed? Were the samples retained for a period of years, and then analyzed after the study was approved, after the method was developed?

Many thanks for your assistance with our understanding of the issues.

Jennifer H. Adams
CFPUA Board of Directors, Vice-Chairman
(910) 784-6498

--

Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering

North Carolina State University

Campus Box 7908

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

SCANNED

WATER TEAM MEETING AGENDA

Wednesday, April 19, 2017

1:00 PM

Drinking Water
Safe - HPA B-1
Water
Main Topic: *KB & San. Remed., PFOS/PROA/PFAS.*

Compliance Issues

Environmental

- Fate of 1,4-dioxane and perfluorinated substances (PFASs) in the urban water cycle
Presented by Detlef Knopp, NC State

Regulation & Policy

✓ CWA Administration

- Security & Emergency Planning
- Communications

✓ SDG

- Compliance Section *Drinking Water - SDG 1/3*
- Laboratory Section *Drinking Water - SDG 2/3*
- Environmental Mgmt. Section *Drinking Water - SDG 3/3*

✓ Operations Dept

- Water Treatment / Surface Water
- Water Treatment / Groundwater
- Water Treatment / AER
- Utility Services / Distribution
- Asset Management

✓ Engineering

- [Water] Project Updates

✓ Public Water Supply

✓ Other Business / Miscellaneous

Next Meeting: May 17, 2017

Adjourn

Adams, Jennifer H

From: Jeremy Blanks <crimson@nc.rr.com>
Sent: Sunday, June 18, 2017 5:00 PM
To: Jennifer.Adams@cfpua.org
Subject: GenX

Mrs Adams,

I found your name connected to the articles on the GenX contamination in the Cape Fear River.

I'm very familiar with GenX as I was the program leader from ~2012 until its completion in ~2014. I also spent 10 years at the DuPont Fayetteville Works site in various technology leadership roles.

I may be of assistance to you as well as local NC officials in the matter. I left Chemours in August of 2015, but have detailed knowledge of this area and the history associated with it.

I have attached a link to my LinkedIn profile below.

<https://www.linkedin.com/in/jeremy-blanks-07b19234>

Please let me know if you would like to discuss.

Best Regards,
Jeremy D Blanks, PhD

From: Mallin, Michael A. [<mailto:mallinm@uncw.edu>]

Sent: Tuesday, November 29, 2016 3:58 PM

To: Polera, Madison Elise <poleram@uncw.edu>; Beth Eckert <Beth.Eckert@cfpua.org>; Cahoon, Larry <cahoon@uncw.edu>; chad.ham@faypwc.com; Deaton, Anne <anne.deaton@ncdenr.gov>; diana_rashash@ncsu.edu; Fitz Rhode <fritz.rohde@noaa.gov>; kemp@cfw.us; kristina.fischer@ncagr.gov; Mike Giles <mikeg@nccoast.org>; Mike Wicker <Mike_Wicker@fws.gov>; nora.deamer@ncdenr.gov; pam.ellis@cfpua.org; janine.harris@noaa.gov; Jennifer Alford <jennifer.b.alford@gmail.com>; slharden@usgs.gov; Saul, Bradley <saalb@live.unc.edu>; Vander Borgh, Mark <mark.vanderborgh@ncdenr.gov>; Prescott, James Carlyle <jcp3677@uncw.edu>
Cc: dyork@dialcordy.com; cmpolera@outlook.com

Subject: recent Cape Fear River paper

Folks – recent CFR paper from NCSU,
Mike

Dr. Michael A. Mallin
Research Professor
Center for Marine Science
University of North Carolina Wilmington
Wilmington, N.C. 28409
Phone: 910 962-2358
Fax: 910 962-2410
Email: mallinm@uncw.edu
Lab website: <http://uncw.edu/cms/aelab/>

DRAFT Relevant FAQs about GenX

June 18, 2017

Who is responsible for establishing drinking water standards?

The Safe Drinking Water Act (SDWA) charges the U.S. Environmental Protection Agency (EPA) to regulate contaminants. That guidance is then passed to state-level agencies, which regulate drinking water providers such as CFPWA.

How does EPA decide which contaminants to regulate?

The SDWA includes a process that EPA must follow to identify and list unregulated contaminants. This process may lead to a change in national drinking water standards. EPA periodically publishes this list of contaminants (called Contaminant Candidate List or CCL) and decides whether to regulate at least five or more contaminants on the list. EPA also uses the CCL to prioritize research and data collection efforts to help the agency determine whether it should regulate a specific contaminant. When EPA regulates a contaminant, public water systems follow that guidance and comply.

Is EPA looking for other unregulated contaminants in the river?

The 1996 SDWA amendments require that once every five years EPA issue a new list of no more than 30 unregulated contaminants to be monitored by public water systems. CFPWA participates in these studies and provides sampling data to EPA. Information from EPA states that the mere presence of contaminants does not necessarily indicate the water poses a health risk.

There are many chemicals, pesticides, pharmaceuticals, hormones and such in water sources. For this reason, it is not uncommon for contaminants such as GenX to be detected in the river. Ultimately, EPA decides which should be monitored and which should be regulated.

Who regulates drinking water providers in North Carolina?

The N.C. Department of Environmental Quality (DEQ) regulates public water systems such as CFPWA. It is Public Water Supply Section of DEQ regulates public water systems within the state and implements mandates of the SDWA.

Who conducted the study that found these contaminants in the Cape Fear River?

The EPA and researchers from N.C. State University and UNC Charlotte collaborated on the study. CFPWA's involvement was generally limited to providing samples from the Sweeney Water Treatment Plant.

When was this study complete and who saw it?

The study was complete in November 2016. EPA participated in the study and presumably was aware of the findings. On November 23, 2016, the report was sent to multiple people at DEQ.

What did CFPUA do next?

Since the report does not state there is an immediate health concern and since EPA commissioned the study and DEQ also had the report, CFPUA staff continued discussion with the researcher to understand whether there are techniques to treat for the compound and with DEQ to determine whether the compound should be regulated. CFPUA not in the position regulatorily or technically to determine whether the compound poses a health threat. The experts at EPA and DEQ make such determinations and then regulate public water systems accordingly.

To help understand the findings, CFPUA invited Dr. Knappe, the N.C. State researcher, to meet with staff on April 19, 2017. He discussed his methodologies, and the collaboration with peers and EPA. He also outlined that he would like to further investigate GenX and look for potential treatment technologies. NCDEQ attended this meeting.

On June 7, 2016, CFPUA sent a letter to DEQ that outlines the study and requests assistance in evaluating implications for the area's source water. On June 9, DEQ responded that EPA is the sole agency responsible for establishing drinking water standards nationwide and that EPA has extensive resources necessary to determine the nature, extent and potential impacts of chemicals such as GenX. They also stated that DEQ is awaiting guidance from EPA that will provide DEQ with the information needed to begin developing regulatory limits for GenX.

Why didn't CFPUA notify the public sooner of GenX?

When staff first became aware of the results, no information indicated there was an immediate health concern. The study concludes the detection of the contaminant and its persistence suggest the need for broader discharge control and contaminant monitoring. Nonetheless, CFPUA invited Dr. Knappe to come review his findings and help them understand next steps from a water treatment perspective. At that time in April, staff didn't know much about GenX as an unregulated contaminant.

The proper people to evaluate and act on potential health effects had the same information. The agencies charged with establishing drinking water standards (EPA), permitting discharges to the river (DEQ) and regulating CFPUA (DEQ) were aware of the same results. With many contaminants in source waters, EPA decides which are a risk and should be regulated. EPA and DEQ have scientists and toxicologist on staff who are charged with making these decisions and then regulating public water systems, and we look to them for guidance.

CFPUA is not qualified to independently assess health risks or determine which contaminants are a concern. As a public water system, CFPUA's focus is on operating its plants and systems in accordance with EPA and DEQ regulations and does not keep epidemiologists or toxicologists on staff. Since there was no indication of an associated health concern, and EPA and DEQ were involved, its mere presence was not unexpected from a public water provider perspective.

No Maximum Contaminant Level (MCL) or similar guidance has been provided by EPA or DEQ. Drinking water standards include an array of substances that have MCLs we must meet in our finished water. We

have a great track record of meeting or exceeding these MCLs. Neither EPA nor DEQ has provided CFPUA guidance regarding GenX.

Why did CFPUA participate in the study?

CFPUA is proud to participate in such studies that advance the water industry. Associated findings will help EPA and DEQ regulate contaminants and ensure source waters are protected.

TO: Cape Fear Public Utility Authority Board of Directors

FROM: Jennifer H. Adams
Robin W. Smith

RE Review of GenX Response

DATE: June 22, 2017

Scope of Report: Review of timeline of the GenX issue; information available to staff of CFPUA; appropriateness of response to the developing information; identification of possible future steps.

I. Timeline of actions related to GenX (attached).



Timeline.doc

II. Background on regulation of GenX. The U.S. Environmental Protection Agency (EPA) began studying the effects of perfluorinated compounds like PFOA and PFOS (used in firefighting foam, water repellants, Teflon, and other products) over fifteen years ago. As concern about health effects and persistence in the environment grew, EPA worked with chemical companies to phase-out the two compounds. In 2000, 3M announced that it would stop production of PFOS. Under a 2006 voluntary agreement with EPA, eight companies committed to phase out PFOA by 2015. As the companies moved to phase-out PFOA and PFOS, they began to develop new compounds like GenX to replace them. Use of new compounds has been phased in within the last 5-10 years.

A. *Safe Drinking Water Act.* Public water systems like Cape Fear Public Utility Authority meet drinking water standards adopted by EPA under the federal Safe Drinking Water Act.

- ◆ EPA has adopted drinking water standards for nearly 90 contaminants; standards do not exist for many compounds used in manufacturing or produced as a by-product of industrial activities. Example: hexavalent chromium
- ◆ EPA has not set drinking water standards for any perfluorinated compounds.

♦ In 2012, EPA required large public water systems to monitor for six unregulated perfluorinated compounds (including PFOA and PFOS) to gather information on the occurrence of those compounds in drinking water and published the results in January 2017. The “unregulated contaminant” monitoring requirement did not cover alternatives like GenX.

♦ Prior to 2016, EPA had a provisional health advisory for PFOA and PFOS (combined) of 600 ng/L based on short-term exposure. On May 25, 2016, EPA issued an updated health advisory for PFOA and PFOS (combined) of 70 parts per trillion (= 70 ng/L) based on life-time exposure. EPA has said the health advisory level does not apply to other PFAS and EPA has not decided whether to adopt a drinking water standard for PFOA and PFOS. That decision would be based on: 1. likelihood the contaminants will be found in drinking water; 2. the health effects of the contaminant; and 3. the technical/economic feasibility of treating the water to reduce any health risk.

B. Clean Water Act Wastewater Discharge Permits

♦ PFAS are not on EPA’s list of priority toxic pollutants

♦ It does not appear that any state has adopted an in-stream water quality standard for PFAS

♦ EPA has set technology-based wastewater limits for individual categories of industries, including chemical plants.

♦ In the absence of an existing EPA limit, the state permit writer can set a limit based on best professional judgment. From the NPDES Permit Writer’s Manual:

“Without applicable effluent guidelines for the discharge or pollutant, permit writers must identify any [limits] on a case-by-case basis, in accordance with the statutory factors specified in CWA sections 301(b)(2) and 304(b).”

III. The 2016 Knappe Paper. In 2015, Cape Fear Public Utility Authority staff agreed to cooperate with Dr. Detlef Knappe of North Carolina State University to look at concentrations of newer fluorinated alternatives (perfluoroalkyl ether carboxylic acids or “PFECAs”) between a known source of fluorochemicals – the Chemours plant in Fayetteville -- and the Sweeney water treatment plant. GenX is a PFECA. The study also looked at the effectiveness of drinking water treatment in removal of those compounds.

For comparison, researchers took raw water samples at two water treatments plants upstream of Chemours– one on the Haw River and the other below Jordan Lake. The research detected older, legacy PFAS (PFOA and PFOS) at the two upstream plants, but very low levels of PFOA/PFOS in raw water at the Sweeney plant. At the Sweeney plant, the sampling detected GenX at an

average concentration of 631 ppt (= 631 ng/L). Six other PFECAs were also detected, but were not quantified.

The Knappe paper noted the lack of published information on the toxicity or environmental fate of PFECAs and the possible need for more work on discharge control and contaminant monitoring. The paper was shared with staff in DEQ's Division of Water Resources and other state and federal agencies.

IV. Findings

CFPUA staff actively participated in the Knappe study to learn more about the possible impact of emerging fluorochemicals on the water supply, as well as their fate in water treatment processes.

The study appears to have been one of the first studies of PFECAs in water supplies. The analytical methods for detecting the compounds were just being developed during the time Dr. Knappe began collecting data in 2013-2014.

The Knappe report provided data on the concentrations of GenX and other PFECAs in the raw water supply, but noted the lack of published information on the toxicity and environmental fate of the contaminants.

EPA has not issued a drinking water standard for PFECAs, so the findings of the Knappe report had no immediate regulatory implications for CFPUA. There was also no health advisory for PFECAs to provide a benchmark for advising the public of any risk.

Discussion of the Knappe report results and next steps resumed in March and April of 2017. CFPUA staff met with Dr. Knappe about a possible follow up study to monitor concentrations of GenX in the water delivery system. CFPUA staff also conferred with NC DEQ about getting the state's assistance to further investigate and regulate the discharge from Chemours.

When the story broke in June of 2017, the CFPUA exec committee was engaged with NC DEQ and requesting assistance in evaluating the effect of GenX on surface water.

V. Conclusion. Given all of the available information, it is our opinion that CFPUA staff acted in an appropriate, professional, timely, and scientific manner. Data was gathered, studied, and reviewed at appropriate levels. Based upon information and facts available to CFPUA at the time, staff moved the issue appropriately through the CFPUA chain of command.

VI. Recommendations

- Consider a process for releasing "non-routine" sampling results to the public.

Sources:

EPA: News release concerning phase-out of PFOS

<https://yosemite.epa.gov/opa/admpress.nsf/0/33aa946e6cb11f35852568e1005246b4>

EPA: Fact sheets on PFOA Stewardship Program <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/fact-sheet-20102015-pfoa-stewardship-program>

EPA: NPDES Permitting of Wastewater Discharges from Chemical Plants

<https://www.epa.gov/eg/organic-chemicals-plastics-and-synthetic-fibers-effluent-guidelines>

EPA Permit Writers Manual: [National Pollutant Discharge Elimination System \(NPDES\) Permit Writers Manual: Chapter 5 - pwm_chapt_05.pdf](#)

EPA: Priority Toxic Pollutant [Toxic and Priority Pollutants Under the Clean Water Act | Effluent Guidelines | US EPA](#)

EPA: Drinking Water Standards [Drinking Water Contaminants – Standards and Regulations | US EPA](#)

EPA: Health Advisories for PFOA and PFOS [Drinking Water Health Advisories for PFOA and PFOS - drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf](#)

EPA: The 3rd Unregulated Contaminant Rule [The Third Unregulated Contaminant Monitoring Rule \(UCMR 3\): Data Summary, January 2017 - ucmr3-data-summary-january-2017.pdf](#)

EPA: Monitoring unregulated contaminants [Monitoring the Occurrence of Unregulated Drinking Water Contaminants | US EPA](#)

EPA: National Primary Drinking Water Standards [National Primary Drinking Water Regulation Table | Ground Water and Drinking Water | US EPA](#)

Legacy and Emerging Perfluoroalkyl Substances are Important Drinking Water Contaminants in the Cape Fear River Watershed of N.C., Detlef Knappe and others, Environmental Science and Technology Letters, Publication date (Web) November 10, 2016.

Documents, including email, between CFPUA and Detlef Knappe related to the National Science Foundation grant application to study perfluoroalkyl substances in the Cape Fear River and development of the study.

CFPUA records, including email, of meetings and other communications following publication of the Knappe paper.

CFPUA GenX Timeline Investigation

	Genesis of the initial study was the interest of NCSU research group (lead by Dr. Detlef Knappe) & EPA collaborators to learn which compound replaced PFOA, the polymer processing aid Dupont/Chemours had been making at the Fayetteville site. No one requested the study. Knappe's recollection is that EPA colleagues first identified GenX as the PFOA replacement in 2012.
6/14/13-10/13/13	Knappe team obtains an analytical standard for GenX and analyzes multiple samples of Sweeney raw water feed. Knappe does not recall if those sample results were provided to CFPUA at that time.
	At this point in time, EPA had a provisional health advisory level of 600 ng/L (PFOA & PFOS combined).
5/30/14	Knappe (NCSU) to Richardson (CFPUA): request for assessment of Sweeney, Brunswick, & Pender for 1,4-dioxane & perfluorinated compound removal. Quick assessment of wide range of treatment technologies.
7/1/14	Knappe to Hawley (CFPUA): confirming NCSU trip to Sweeney; no confirmation from Brunswick (Glenn Walker) ; Pender expressed interest (Brandon Garner)
8/13/14	Knappe to Hawley: confirmed sampling visit on 8/18 for purposes of collecting a few water samples for 1,4-dioxane & polyfluorinated ether analysis. Samples collection proposed from various unit ops in water treatment process.
8/18/14	Sampling of unit processes through the Sweeney WTP was completed by Knappe's team.
10/13/14	Knappe to Richardson: Knappe writing a proposal to NSF to study the occurrence of fluorochemicals in the CF River and to assess/develop treatment options. Offered co-principal investigator status to Richardson.
6/10/15	Richardson to Knappe: Confirmed study participation and co-PI status; goal to closely collaborate to facilitate knowledge transfer.
8/26/15	Richardson to Flechtner: Knappe NSF proposal sent for approval. Goal of study: "Because of their persistence, bioaccumulation potential and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are being replaced with short-chain PFASs and fluorinated alternatives. Almost no information exists about the occurrence of fluorinated alternatives and their behavior during water treatment. The overall goal of the proposed research is to begin to fill this knowledge gap by studying one class of fluorinated alternatives, perfluoro(poly)ethers (PFPEs). Research objectives include (1) develop a method for analysis... (3) apply the method to Sweeney WTP samples.... Results are expected to provide the basis for a broader investigation of the behavior of fluorinated alternatives in natural and engineered systems."
	Consider this to be a second study to confirm the presence of additional perfluoroalkyl ether carboxylic acids (PFECAs). GenX is only one type of PFECAs, there are 3 others as well.
8/26/15	Knappe to Flechtner, Richardson: email re: collaborative project between NCSU & CFPUA. Goal is to study the fate of perfluorinated ethers in the CFR from the point of discharge near Fayetteville to your drinking water intake. In addition, we are planning to evaluate the treatment effectiveness of individual unit processes at the Sweeney WTP. Mike is a co-PI on the project.
8/27/15	Signed agreement returned to Knappe from Flechtner, "This looks like an interesting and valuable study and I look forward to seeing the findings."
5/3/16	Knappe to Richardson/Kearns: share beginnings of paper on occurrence of perfluoroalkyl substances in CFR. Contained with abstract "The only PFECA for which an authentic standard was available for quantification, GenX, was detected at an average concentration at 631 ng/L."
5/25/16	EPA reduces the health advisory limit for PFOA & PFOS to 70 ng/L.
9/12/16	Richardson & Styers meeting; reviewed Knappe report. "Good thing to be published and get

	information out there on emerging contaminants.”
9/18/16	Knappe to Kearns, Richardson, and 3 other study participants: Will be sending manuscript to Environmental Science & Technology Letters on 9/26/16. Includes occurrence data for perfluorinated compounds. Sent draft research paper; requested final comments before publication submission on 9/26/16.
9/24/16	Knappe to Kearns, Richardson: interest in co-authorship on paper? Response “Yes, grateful if you added us as co-authors. Do not have any comments on it at this time”. Added as co-authors since they provided samples.
9/30/16	Richardson retires from CFPUA
11/10/16	Knappe paper published in Environmental Science & Technology Letters, “Legacy & Emerging Perfluoroalkyl Substances are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina”. Co-authors include CFPUA, US EPA, Town of Pittsboro, and Fayetteville Public Works Commission. Study found that for PFAS compounds, which the EPA had already established health advisories for, were not found at high levels in the CFR. The paper also indicated that there was little information on the toxicity of the fluorochemical alternatives (PFECAs) found in the CFR, and that EPA has not established a health advisory standard for those PFECAs.
11/23/16	Knappe forwards published paper to multiple individuals within NC DEQ and various cities (CFPUA not included in email). Text of email includes “attaching a paper we published this month in ES&T Letters. We studied the occurrence of per- and polyfluoroalkyl substances (PFAS) in the Cape Fear River watershed. Legacy PFAS, such as PFOA and PFOS dominated the PFAS signature in the Haw River, In contrast, new fluorinated alternatives such as GenX, a replacement for PFOA, were very high in Wilm (and by association also in Brunswick and Pender). None of the newly discovered compounds being discharged by the Chemours plant south of Fayetteville are removed by the advanced and conventional treatment processes employed in the Sweeney WTP in Wilm. Also, many of the compounds are essentially non-adsorbable on activated carbon. I think it would be useful to discuss the results. A large number of people are exposed to high levels of PFAS through their drinking water!”
11/29/16	Dr. Mallin (UNCW) sends email stating “Folks – recent CFR paper from NCSU”, with attached published paper. Recipients include personnel from UNCW, NC DENR, NOAA, NCSU, Fayetteville Public Works, CFPUA (Eckert & Ellis), Cape Fear River Watch & NC Coastal Federation
3/6/17	Knappe sends published paper to Kearns
3/7/17	Kearns forwards paper to Eckert, Deaney, & Allyson Ridout (all CFPUA internal).
3/7/17	Kearns to Deaney: would be good to investigate whether a lab can analyze for emerging compounds highlighted in study.
3/20/17	Styers, Eckert, Vandermeiden, and Flechtner meet to discuss Knappe paper. Determined that more information was needed and that Knappe needed to provide next steps. Styers requested Kearns coordinate this request.
4/13/17	Styers, Eckert, Malone & Kearns meet to discuss Knappe’s desire for more research, pros, cons, and what CFPUA needed Knappe to provide to improve CFPUA’s understanding of the previous paper and next steps.
4/13/17	Kearns to Water Team, inviting team to April 19th meeting with Knappe. Invitees include Flechtner, Styers, Vandermeiden, Heidi Cox (DEQ), McGill, Eckert, and others. Purpose “Been approached by Knappe re: legacy & emerging PFAS compounds in our raw water and their fate once they have passed through the Sweeney WTP treatment regime. Due to their persistent nature and potential concentrations in our source water, there is a strong desire to identify the PFAS compounds, their

	concentrations, and their fate in our treatment plants through a coordinated sampling effort with Detlef's lab. Proposal attached. The scope of this project is such that thorough vetting and buy-in from all Authority levels would be best before anything moves forward."
4/19/17	Water Team Mtg with Knappe. CFPUA staff in attendance (minus Flechtner), as well as Heidi Cox, NC DEQ. Reviewed study results; proposed additional sampling to determine the fate of 1,4-dioxane and perfluoroalkyl substances (PFAS) in the urban water cycle (source -> water system -> distribution -> wastewater -> discharge). Determine fate of 1,4-dioxane & PFAS during ASR; determine possible association of 1,4-dioxane & PFAS with biosolids. Knappe wanted to get other utilities involved in sampling. Knappe wanted his next project to further investigate GenX and its fate and look for potential treatment technologies and to use the research to talk to the state to get it regulated and out of the river.
	Knappe to Styers: "Not enough information to say that you shouldn't drink the water"
	CFPUA staff continues to research GenX and PFOAs and its human health effects. Conflicting information is found; most information stated more information and study is needed to determine what if any health effects are associated with the product.
4/22/17	Knappe forwards abstract (Swedish study) re: GenX toxicity to Kearns, "which purports that GenX is more toxic than PFOA, concentrations in Wilm, Brunswick, & Pender greatly exceed the current health advisory level for PFOA. I think it is important that we push to dramatically reduce inputs of GenX and similar compounds into the CFR".
4/26/17	Eckert requests Chemours NPDES permit from NC DEQ
5/2/17	Eckert discusses issue with Linda Culpepper, DEQ, at ESI mtg. Asks about the process CFPUA would use to get the state's assistance to further investigate and regulate the discharge of new chemicals from Chemours facility. Given the name of a contact in the DEQ Fayetteville Regional Office.
	CFPUA staff draft letter for NC DEQ, will seek board approval.
5/15/17	Star News inquiry to Knappe, forwarded to Kearns & Eckert
6/1/17	CFPUA contacted by StarNews re: Knappe study. Styers discussed with Haggerty and provided answers the next day.
6/5/17	Styers sent email to BOD about upcoming article in StarNews.
6/7/17	CFPUA Exec Committee Mtg: Flechtner brought issue to committee mtg. Styers summarized Knappe report. Mentioned StarNews would be doing article. Committee approved a letter to DEQ, including research paper, requesting DEQ assistance in evaluating the effect of the substance on surface water. No information presented that indicated a health concern. EPA proposed study and they set national drinking water standards. DEQ regulates based on those standards.
6/8/17	StarNews article published.

Interviewees:

Ben Kearns, CFPUA Water Operations Supervisor
John Malone, CFPUA Water Treatment Plant Supervisor
Frank Styers, CFPUA Chief Operations Officer
Beth Eckert, CFPUA Environmental Management Director
Jim Flechtner, CFPUA Executive Director
Linda Miles, CFPUA Consulting Attorney
Mike Brown, CFPUA Board Chairman
Dr. Detlef Knappe, NCSU

Prepared by:

Jennifer H Adams, PE, CFPUA Board Vice-Chairman

Robin Smith, JD, Robin Smith Law Office

6/20/17

John Malone

From: Frank Styers
Sent: Friday, June 16, 2017 2:50 PM
To: John Malone; b@cfpua5.onmicrosoft.com
Subject: Fwd: PFASs in the Cape Fear River watershed
Attachments: PFECAs_Sun_ESTL2016.pdf; ATT00001.htm; PFECAs_Sun_ESTL2016_SI.pdf; ATT00002.htm

Sent from my iPhone

Begin forwarded message:

From: "Detlef Knappe" <knappe@ncsu.edu>
To: "Frank Styers" <Frank.Styers@cfpua.org>
Subject: Fwd: PFASs in the Cape Fear River watershed

Frank,

I also sent this email.

Detlef

----- Forwarded Message -----

Subject: PFASs in the Cape Fear River watershed

Date: Wed, 23 Nov 2016 11:46:03 -0500

From: Detlef Knappe <knappe@ncsu.edu>

To: Hill, Tammy <tammy.l.hill@ncdenr.gov>, Adam Pickett <apickett@pittsboronc.gov>, aobriant@harnett.org <aobriant@harnett.org>, Austin, Vardry E <vardry.austin@ncdenr.gov>, Brower, Connie <connie.brower@ncdenr.gov>, Godreau, Jessica <jessica.godreau@ncdenr.gov>, Gore, Deborah <deborah.gore@ncdenr.gov>, Grzyb, Julie <julie.grzyb@ncdenr.gov>, Ham, Chad <chad.ham@faypwc.com>, Manning, Jeff <jeff.manning@ncdenr.gov>, Johnson, Chris <chris.johnson@ncdenr.gov>, Martie Groome <martie.groome@greensboro-nc.gov>, Michele Dawes <MDAWES@ci.asheboro.nc.us>, Poupart, Jeff <jeff.poupart@ncdenr.gov>, Risgaard, Jon <jon.risgaard@ncdenr.gov>, Sadosky, Rebecca <rebecca.sadosky@ncdenr.gov>, UCFRBA Kevin Eason <keason@ci.reidsville.nc.us>, UCFRBA Michael Rhone <mrhoney@ci.asheboro.nc.us>, Mick Noland <mick.noland@faypwc.com>
CC: Karoly, Cyndi <cyndi.karoly@ncdenr.gov>, Zimmerman, Jay <jay.zimmerman@ncdenr.gov>, Knight, Sherri <sherri.knight@ncdenr.gov>, Smith, Danny <danny.smith@ncdenr.gov>, Gregson, Jim <jim.gregson@ncdenr.gov>, Henson, Belinda <belinda.henson@ncdenr.gov>, Kroeger, Steve <steve.kroeger@ncdenr.gov>, tom.reeder@ncdenr.gov

Hello everyone,

I am attaching a paper we published this month in ES&T Letters. We studied the occurrence of per- and polyfluoroalkyl substances (PFASs) in the Cape Fear River watershed. Legacy PFASs, such as PFOA and PFOS dominated the PFAS signature in the Haw River. In contrast, new

fluorinated alternatives such as GenX, a replacement for PFOA, were very high in Wilmington (and by association also in Brunswick and Pender). None of the newly discovered compounds being discharged by the Chemours plant south of Fayetteville are removed by the advanced and conventional treatment processes employed in the Sweeney WTP in Wilmington. Also, many of the compounds are essentially non-adsorbable on activated carbon. I think it would be useful to discuss the results. A large number of people are exposed to high levels of PFASs through their drinking water!

Best regards,

Detlef

On 9/23/16 9:50 AM, Hill, Tammy wrote:

Hello!

I think you all know that Carrie Ruhlman has moved on from DWR. I'll be taking over coordination of the 1,4-dioxane monitoring project. Please feel free to contact me if I can be of assistance in this regard.

Attached are the results from DWR's quarterly surface water monitoring from January-July 2016. We will sample again in October, then prepare a summary report for October 2014-October 2016 data by the end of the year.

Warm regards,

Tammy Hill

Water Quality Data Analyst
NC Division of Water Resources – Water Sciences Section
NC Department of Environmental Quality

919 743 8412 office
919 743 8517 fax
Tammy.L.Hill@ncdenr.gov

1623 Mail Service Center
Raleigh, NC 27699-1623



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Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

• Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

TESTING REQUIREMENTS FOR ORGANIC TOXIC POLLUTANTS INDUSTRY CATEGORY*

INDUSTRY CATEGORY	GC/MS FRACTION ¹			
	Volatile	Acid	Base/Neutral	Pesticide
Adhesives and sealants.....	X	X	X	-
Aluminum forming.....	X	X	X	-
Auto and other laundries.....	X	X	X	X
Battery manufacturing.....	X	-	X	-
Coal mining.....	X	X	X	X
Coil coating.....	X	X	X	-
Copper forming.....	X	X	X	-
Electric and electronic compounds.....	X	X	X	X
Electroplating.....	X	X	X	-
Explosives manufacturing.....	-	X	X	-
Foundries.....	X	X	X	-
Gum and wood chemicals.....	X	X	X	X
Inorganic chemicals manufacturing.....	X	X	X	-
Iron and steel manufacturing.....	X	X	X	-
Leather tanning and finishing.....	X	X	X	X
Mechanical products manufacturing.....	X	X	X	-
Nonferrous metals manufacturing.....	X	X	X	X
Ore mining.....	X	X	X	X
Organic chemicals manufacturing.....	X	X	X	X
Paint and ink formulation.....	X	X	X	X
Pesticides.....	X	X	X	X
Petroleum refining.....	X	X	X	X
Pharmaceutical preparations.....	X	X	X	-
Photographic equipment and supplies.....	X	X	X	X
Plastic and synthetic materials manufacturing.....	X	X	X	X
Plastic processing.....	X	-	-	-
Porcelain enameling.....	X	-	X	X
Printing and publishing.....	X	X	X	X
Pulp and paperboard mills.....	X	X	X	X
Rubber processing.....	X	X	X	-
Soap and detergent manufacturing.....	X	X	X	-
Steam electric power plants.....	X	X	X	-
Textile mills.....	X	X	X	X
Timber products processing.....	X	X	X	X

*See note at conclusion of 40 CFR Part 122, Appendix D (1983) for explanation of effect of suspensions on testing requirements for primary industry categories.

¹The pollutants in each fraction are listed in Item V-C.

X = Testing required.

- = Testing not required.

NPDES permitting instructions

**TOXIC POLLUTANTS AND HAZARDOUS SUBSTANCES
REQUIRED TO BE IDENTIFIED BY APPLICANTS IF EXPECTED TO BE PRESENT**

TOXIC POLLUTANT	HAZARDOUS SUBSTANCES	HAZARDOUS SUBSTANCES
Asbestos	Dichlorvos	Naled
HAZARDOUS SUBSTANCES	Diethyl amine	Napthenic acid
Acetaldehyde	Dimethyl amine	Nitrotoluene
Allyl alcohol	Dinitrobenzene	Parathion
Allyl chloride	Diquat	Phenolsulfonate
Amyl acetate	Disulfoton	Phosgene
Aniline	Diuron	Propargite
Benzonitrile	Epichlorohydrin	Propylene oxide
Benzyl chloride	Ethion	Pyrethrins
Butyl acetate	Ethylene diamine	Quinoline
Butylamine	Ethylene dibromide	Resorcinol
Captan	Formaldehyde	Strontium
Carbaryl	Furfural	Strychnine
Carbofuran	Guthion	Styrene
Carbon disulfide	Isoprene	2,4,5-T (2,4,5-Trichlorophenoxyacetic acid)
Chlorpyrifos	Isopropanolamine	TDE (Tetrachlorodiphenyl ethane)
Coumaphos	Kelthane	2,4,5-TP [2-(2,4,5-Trichlorophenoxy) propanoic acid]
Cresol	Kepone	Trichlorofon
Crotonaldehyde	Malathion	Triethanolamine
Cyclohexane	Mercaptodimethur	Triethylamine
2,4-D (2,4-Dichlorophenoxyacetic acid)	Methoxychlor	Trimethylamine
Diazinon	Methyl mercaptan	Uranium
Dicamba	Methyl methacrylate	Vanadium
Dichlobenil	Methyl parathion	Vinyl acetate
Dichlone	Mevinphos	Xylene
2,2-Dichloropropionic acid	Mexacarbate	Xylenol
	Monoethyl amine	Zirconium
	Monomethyl amine	

HAZARDOUS SUBSTANCES

1. Acetaldehyde	74. Carbaryl	145. Formaldehyde
2. Acetic acid	75. Carbofuran	146. Formic acid
3. Acetic anhydride	76. Carbon disulfide	147. Fumaric acid
4. Acetone cyanohydrin	77. Carbon tetrachloride	148. Furfural
5. Acetyl bromide	78. Chlordane	149. Guthion
6. Acetyl chloride	79. Chlorine	150. Heptachlor
7. Acrolein	80. Chlorobenzene	151. Hexachlorocyclopentadiene
8. Acrylonitrile	81. Chloroform	152. Hydrochloric acid
9. Adipic acid	82. Chloropyrifos	153. Hydrofluoric acid
10. Aldrin	83. Chlorosulfonic acid	154. Hydrogen cyanide
11. Allyl alcohol	84. Chromic acetate	155. Hydrogen sulfide
12. Allyl chloride	85. Chromic acid	156. Isoprene
13. Aluminum sulfate	86. Chromic sulfate	157. Isopropanolamine
14. Ammonia	87. Chromous chloride	dodecylbenzenesulfonate
15. Ammonium acetate	88. Cobaltous bromide	158. Kelthane
16. Ammonium benzoate	89. Cobaltous formate	159. Kepone
17. Ammonium bicarbonate	90. Cobaltous sulfamate	160. Lead acetate
18. Ammonium bichromate	91. Coumaphos	161. Lead arsenate
19. Ammonium bifluoride	92. Cresol	162. Lead chloride
20. Ammonium bisulfite	93. Crotonaldehyde	163. Lead fluoborate
21. Ammonium carbamate	94. Cupric acetate	164. Lead flourite
22. Ammonium carbonate	95. Cupric acetoarsenite	165. Lead iodide
23. Ammonium chloride	96. Cupric chloride	166. Lead nitrate
24. Ammonium chromate	97. Cupric nitrate	167. Lead stearate
25. Ammonium citrate	98. Cupric oxalate	168. Lead sulfate
26. Ammonium fluoroborate	99. Cupric sulfate	169. Lead sulfide
27. Ammonium fluoride	100. Cupric sulfate ammoniated	170. Lead thiocyanate
28. Ammonium hydroxide	101. Cupric tartrate	171. Lindane
29. Ammonium oxalate	102. Cyanogen chloride	172. Lithium chromate
30. Ammonium silicofluoride	103. Cyclohexane	173. Malathion
31. Ammonium sulfamate	104. 2,4-D acid (2,4- Dichlorophenoxyacetic acid)	174. Maleic acid
32. Ammonium sulfide	105. 2,4-D esters (2,4- Dichlorophenoxyacetic acid esters)	175. Maleic anhydride
33. Ammonium sulfite	106. DDT	176. Mercaptodimethur
34. Ammonium tartrate	107. Diazinon	177. Mercuric cyanide
35. Ammonium thiocyanate	108. Dicamba	178. Mercuric nitrate
36. Ammonium thiosulfate	109. Dichlobenil	179. Mercuric sulfate
37. Amyl acetate	110. Dichlone	180. Mercuric thiocyanate
38. Aniline	111. Dichlorobenzene	181. Mercurous nitrate
39. Antimony pentachloride	112. Dichloropropane	182. Methoxychlor
40. Antimony potassium tartrate	113. Dichloropropene	183. Methyl mercaptan
41. Antimony tribromide	114. Dichloropropene-dichloropropane mix	184. Methyl methacrylate
42. Antimony trichloride	115. 2,2-Dichloropropionic acid	185. Methyl parathion
43. Antimony trifluoride	116. Dichlorvos	186. Mevinphos
44. Antimony trioxide	117. Dieldrin	187. Mexacarbate
45. Arsenic disulfide	118. Diethylamine	188. Monoethylamine
46. Arsenic pentoxide	119. Dimethylamine	189. Monomethylamine
47. Arsenic trichloride	120. Dinitrobenzene	190. Naled
48. Arsenic trioxide	121. Dinitrophenol	191. Naphthalene
49. Arsenic trisulfide	122. Dinitrotoluene	192. Naphthenic acid
50. Barium cyanide	123. Diquat	193. Nickel ammonium sulfate
51. Benzene	124. Disulfoton	194. Nickel chloride
52. Benzoic acid	125. Diuron	195. Nickel hydroxide
53. Benzonitrile	126. Dodecylbenzenesulfonic acid	196. Nickel nitrate
54. Benzoyl chloride	127. Endosulfan	197. Nickel sulfate
55. Benzyl chloride	128. Endrin	198. Nitric acid
56. Beryllium chloride	129. Epichlorohydrin	199. Nitrobenzene
57. Beryllium fluoride	130. Ethion	200. Nitrogen dioxide
58. Beryllium nitrate	131. Ethylbenzene	201. Nitrophenol
59. Butylacetate	132. Ethylenediamine	202. Nitrotoluene
60. n-Butylphthalate	133. Ethylene dibromide	203. Paraformaldehyde
61. Butylamine	134. Ethylene dichloride	204. Parathion
62. Butyric acid	135. Ethylene diaminetetracetic acid (EDTA)	205. Pentachlorophenol
63. Cadmium acetate	136. Ferric ammonium citrate	206. Phenol
64. Cadmium bromide	137. Ferric ammonium oxalate	207. Phosgene
65. Cadmium chloride	138. Ferric chloride	208. Phosphoric acid
66. Calcium arsenate	139. Ferric fluoride	209. Phosphorus
67. Calcium arsenite	140. Ferric nitrate	210. Phosphorus oxychloride
69. Calcium carbide	141. Ferric sulfate	211. Phosphorus pentasulfide
69. Calcium chromate	142. Ferrous ammonium sulfate	212. Phosphorus trichloride
70. Calcium cyanide	143. Ferrous chloride	213. Polychlorinated biphenyls (PCB)
71. Calcium dodecylbenzenesulfonate	144. Ferrous sulfate	214. Potassium arsenate
72. Calcium hypochlorite		215. Potassium arsenite
73. Captan		216. Potassium bichromate

Table 2C-4

HAZARDOUS SUBSTANCES

217. Potassium chromate	247. Sodium selenite	270. Trimethylamine
218. Potassium cyanide	248. Strontium chromate	271. Uranyl acetate
219. Potassium hydroxide	249. Strychnine	272. Uranyl nitrate
220. Potassium permanganate	250. Styrene	273. Vanadium pentoxide
221. Propargite	251. Sulfuric acid	274. Vanadyl sulfate
222. Propionic acid	252. Sulfur monochloride	275. Vinyl acetate
223. Propionic anhydride	253. 2,4,5-T acid (2,4,5-Trichlorophenoxyacetic acid)	276. Vinylidene chloride
224. Propylene oxide	254. 2,4,5-T amines (2,4,5-Trichlorophenoxy acetic acid amines)	277. Xylene
225. Pyrethrins	255. 2,4,5-T esters (2,4,5 Trichlorophenoxy acetic acid esters)	278. Xylenol
226. Quinoline	256. 2,4,5-T salts (2,4,5-Trichlorophenoxy acetic acid salts)	279. Zinc acetate
227. Resorcinol	257. 2,4,5-TP acid (2,4,5-Trichlorophenoxy propanoic acid)	280. Zinc ammonium chloride
228. Selenium oxide	258. 2,4,5-TP acid esters (2,4,5-Trichlorophenoxy propanoic acid esters)	281. Zinc borate
229. Silver nitrate	259. TDE (Tetrachlorodiphenyl ethane)	282. Zinc bromide
230. Sodium	260. Tetraethyl lead	283. Zinc carbonate
231. Sodium arsenate	261. Tetraethyl pyrophosphate	284. Zinc chloride
232. Sodium arsenite	262. Thallium sulfate	285. Zinc cyanide
233. Sodium bichromate	263. Toluene	286. Zinc fluoride
234. Sodium bifluoride	264. Toxaphene	287. Zinc formate
235. Sodium bisulfite	265. Trichlorofon	288. Zinc hydrosulfite
236. Sodium chromate	266. Trichloroethylene	289. Zinc nitrate
237. Sodium cyanide	267. Trichlorophenol	290. Zinc phenolsulfonate
238. Sodium dodecylbenzenesulfonate	268. Triethanolamine	291. Zinc phosphide
239. Sodium fluoride	269. Triethylamine	292. Zinc silicofluoride
240. Sodium hydrosulfide		293. Zinc sulfate
241. Sodium hydroxide		294. Zirconium nitrate
242. Sodium hypochlorite		295. Zirconium potassium fluoride
243. Sodium methylate		296. Zirconium sulfate
244. Sodium nitrite		297. Zirconium tetrachloride
245. Sodium phosphate (dibasic)		
246. Sodium phosphate (tribasic)		

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,^{*,†,‡,§} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||} Adam Pickett,[‡] Chris Smith,[#] and Detlef R. U. Knappe[‡]

[†]Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

[‡]Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[§]National Exposure Research Laboratory, U.S. Environmental Protection Agency Research, Triangle Park, North Carolina 27711, United States

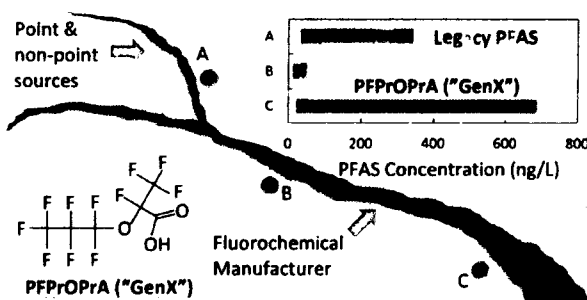
^{||}Cape Fear Public Utility Authority, Wilmington, North Carolina 28403, United States

[‡]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypyranoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n = 37$). Six other PFECAs were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain perfluoroalkyl sulfonic acids [$\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$; $n \geq 6$ (PFASs)] and perfluoroalkyl carboxylic acids [$\text{C}_n\text{F}_{2n+1}\text{COOH}$; $n \geq 7$ (PFCAs)] were predominantly used.² Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs^{3,4} has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health

advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.^{5,6} Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.^{7–10} Some fluorinated alternatives were recently identified,^{8,11} but others remain unknown^{12–14} because they are either proprietary or manufacturing byproducts.

Received: October 13, 2016

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One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.¹¹ Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro-(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA), and perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA alternative¹⁵ that has been produced since 2010 with the trade name "GenX". To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,¹⁵ and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),^{16–20} little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C–F bond makes PFASs refractory to abiotic and biotic degradation,²¹ and most water treatment processes are ineffective for legacy PFAS removal.^{22–27} Processes capable of removing PFCAs and PFSA s include nanofiltration,²⁸ reverse osmosis,²⁵ ion exchange,^{28,29} and activated carbon adsorption,^{28,29} with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on powdered activated carbon (PAC).

MATERIALS AND METHODS

Water Samples. Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train [raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 20 L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4 °C until use in PAC adsorption experiments (background water matrix characteristics listed in Table S3).

Adsorption Experiments. Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 10–800%

of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 ppm) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 μ m, BET surface area of 1460 m²/g)³⁰ proven to be effective for PFAS removal in a prior study²⁹ was used at doses of 30, 60, and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

PFAS Analysis. Information about analytical standards and liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods for PFAS quantification is provided in the Supporting Information.

RESULTS AND DISCUSSION

Occurrence of PFASs in Drinking Water Sources. Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1.

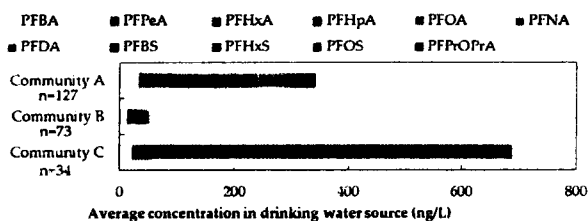


Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean Σ PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,³¹ suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80–85% C_nF_{2n+1}COOH; $n = 7–9$) in 2006 to short-chain (76% C_nF_{2n+1}COOH; $n = 5–6$) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.

Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QLS, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QLS. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.³² However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

Fate of PFASs in Conventional and Advanced Water Treatment Processes. To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.^{22–26} The data further illustrate that no measurable PFECA removal occurred in this DWTP. Concentrations of some PFCAs, PFSAs, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.²⁵ Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400–500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2–113 times greater than that of PFPrOPrA (Figure 2b).

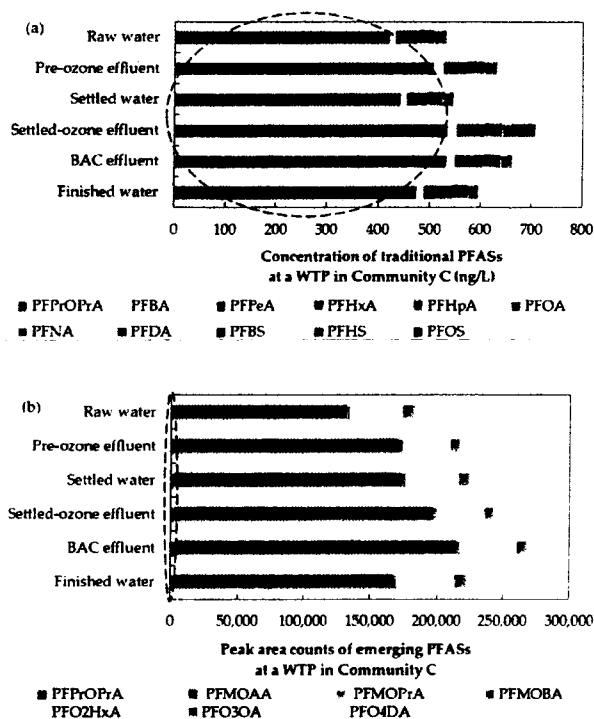


Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QLS were not plotted.

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

Adsorption of PFASs by PAC. PAC can effectively remove long-chain PFCAs and PFSAs, but its effectiveness decreases with decreasing PFAS chain length.^{24,25,29} It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥ 7 . At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSAs were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous

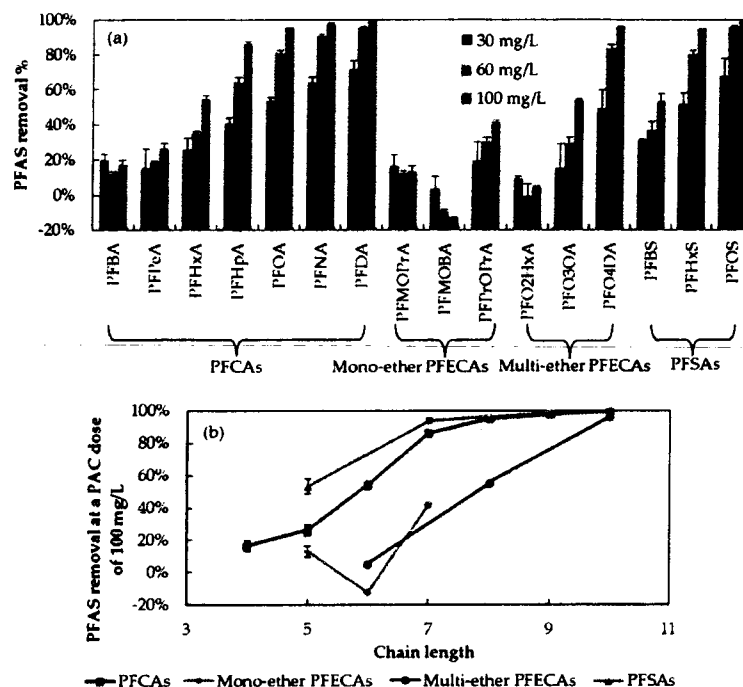


Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ~ 1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

studies.^{24,25,29} PFECAs exhibited adsorbabilities lower than those of PFCAs of the same chain length (e.g., PFMObA < PFHxA), suggesting that the replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional CF_2 groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMObA \sim PFO2HxA, PFPrOPrA \sim PFO3OA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMObA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFCA removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: msun8@unc.edu. Phone: 704-687-1723.

ORCID

Mei Sun: 0000-0001-5854-9862

Notes

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

The authors declare no competing financial interest.

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Supporting information

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Supporting information includes analytical method description, 6 tables, and 5 figures.

Mei Sun^{1,2,*}, Elisa Arevalo², Mark Strynar³, Andrew Lindstrom³, Michael Richardson⁴, Ben
Kearns⁴, Adam Pickett⁵, Chris Smith⁶, and Detlef R.U. Knappe²

¹Department of Civil and Environmental Engineering
University of North Carolina at Charlotte
Charlotte, North Carolina 28223, USA

²Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Raleigh, North Carolina 27695, USA

³National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711, USA

⁴Cape Fear Public Utility Authority
Wilmington, North Carolina 28403, USA

⁵Town of Pittsboro
Pittsboro, North Carolina 27312, USA

⁶Fayetteville Public Works Commission
Fayetteville, North Carolina 28301, USA

*Corresponding Author Email: msun8@uncc.edu; Phone: 704-687-1723

Analytical standards: PFASs studied in this research are listed in Table S1. For legacy PFASs, native and isotopically labeled standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA). No analytical standards were available for other PFECAs.

PFAS quantification: PFAS concentrations in samples from DWTPs and adsorption tests were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using a large-volume (0.9 mL) direct injection method. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC-MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5 μ m 100Å, Phenomenex Inc.) was used for PFAS analysis. The eluent gradient is shown in Table S4 in SI. All samples, calibration standards, and quality control samples were spiked with isotopically labeled internal standards, filtered through 0.45- μ m glass microfiber syringe filters, and analyzed in duplicate. The MS transitions for PFAS analytes and internal standards are shown in Table S5 in SI. The quantitation limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid, and 10 ng/L for other legacy PFASs and PFPrOPrA. The QL was defined as the first point of the standard curve, for which the regression equation yielded a calculated value within $\pm 30\%$ error. For PFECAs without analytical standards, chromatographic peak areas are reported.

PFAS concentrations along the treatment train of DWTP C were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Method details are described elsewhere.¹ The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAs without standards.

Table S1. Perfluoroalkyl substances (PFASs) detected in the Cape Fear River (CFR) watershed

Compound	Molecular weight	Formula	CAS #	# of perfluorinated carbons	Chain length (including all C, O and S)
Perfluorocarboxylic acids (PFCAs)					
Perfluorobutanoic acid (PFBA)	214.0	C ₄ HF ₇ O ₂	375-22-4	3	4
Perfluoropentanoic acid (PFPeA)	264.0	C ₅ HF ₉ O ₂	2706-90-3	4	5
Perfluorohexanoic acid (PFHxA)	314.1	C ₆ HF ₁₁ O ₂	307-24-4	5	6
Perfluoroheptanoic acid (PFHpA)	364.1	C ₇ HF ₁₃ O ₂	375-85-9	6	7
Perfluorooctanoic acid (PFOA)	414.1	C ₈ HF ₁₅ O ₂	335-67-1	7	8
Perfluorononanoic acid (PFNA)	464.1	C ₉ HF ₁₇ O ₂	375-95-1	8	9
Perfluorodecanoic acid (PFDA)	514.1	C ₁₀ HF ₁₉ O ₂	335-76-2	9	10
Perfluorosulfonic acids (PFSAAs)					
Perfluorobutane sulfonic acid (PFBS)	300.1	C ₄ HF ₉ SO ₃	375-73-5	4	5
Perfluorohexane sulfonic acid (PFHxS)	400.1	C ₆ HF ₁₃ SO ₃	355-46-4	6	7
Perfluorooctane sulfonic acid (PFOS)	500.1	C ₈ HF ₁₇ SO ₃	1763-23-1	8	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)					
Perfluoro-2-methoxyacetic acid (PFMOAA)	180.0	C ₃ HF ₅ O ₃	674-13-5	2	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	230.0	C ₄ HF ₇ O ₃	377-73-1	3	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)	280.0	C ₅ HF ₉ O ₃	863090-89-5	4	6
Perfluoro-2-propoxypropanoic acid (PFPrOPrA)	330.1	C ₆ HF ₁₁ O ₃	13252-13-6	5	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	246.0	C ₄ HF ₇ O ₄	39492-88-1	3	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	312.0	C ₅ HF ₉ O ₅	39492-89-2	4	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	378.1	C ₆ HF ₁₁ O ₆	39492-90-5	5	10

Table S2. Operational conditions of DWTP C on sampling day (August 18, 2014)

Parameter	Value
Raw water ozone dose	3.1 mg/L
Raw water total organic carbon concentration	6.0 mg/L
Aluminum sulfate coagulant dose	43 mg/L
Coagulation pH	5.70
Settled water ozone dose	1.3 mg/L
Settled water total organic carbon concentration	1.90 mg/L
Empty bed contact time in biological activated carbon filters	9.4 minutes for granular activated carbon layer 2.3 minutes for sand layer
Medium pressure UV dose	25 mJ/cm ²
Free chlorine dose	1.26 mg/L as Cl ₂
Free chlorine contact time	17.2 hours

Table S3. Water quality characteristics of surface water used in adsorption tests

Non-purgeable organic carbon (mg/L)	Ultraviolet absorbance at a wavelength of 254 nm	pH	Alkalinity (mg/L as CaCO ₃)	Conductivity (uS/cm)
9.036	0.399	7.53	19	133.5

Table S4. LC gradient method for PFAS analysis

Time (min)	Mobile Phase A% (v/v)	Mobile Phase B%	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mobile phase A: 2 mM ammonium acetate in ultrapure water with 5% methanol

Mobile phase B: 2 mM ammonium acetate in acetonitrile with 5% ultrapure water

Table S5. MS transitions for PFAS Analysis

	Compound	MS/MS Transition	Internal standard
Legacy PFASs	PFBA	212.8 → 168.8	13C4-PFBA
	PFPeA	262.9 → 218.8	13C2- PFHxA
	PFHxA	313.6 → 268.8	13C2- PFHxA
	PFHpA	362.9 → 318.8	13C4- PFOA
	PFOA	413.0 → 368.8	13C4- PFOA
	PFNA	463.0 → 418.8	13C4- PFOA
	PFDA	513.1 → 68.8	13C2-PFDA
	PFBS	299.1 → 98.8	18O2-PFHxS
	PFHxS	399.1 → 98.8	18O2-PFHxS
	PFOS	498.9 → 98.8	13C4-PFOS
PFECAs	PFMOAA	180.0 → 85.0	N/A
	PFMOPrA	229.1 → 184.9	N/A
	PFMOBA	279.0 → 234.8	N/A
	PFPrOPrA	329.0 → 284.7	13C2- PFHxA
	PFO2HxA	245.1 → 85.0	N/A
	PFO3OA	311. → 84.9	N/A
	PFO4DA	377.1 → 85.0	N/A
Internal standards	Perfluoro-n-[1,2,3,4- ¹³ C ₄]butanoic acid (13C4-PFBA)	217.0 → 172	Not applicable
	Perfluoro-n-[1,2- ¹³ C ₂]hexanoic acid (13C2-PFHxA)	315.1 → 269.8	
	Perfluoro-n-[1,2,3,4- ¹³ C ₂]octanoic acid (13C4-PFOA)	417.0 → 372.0	
	Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid (13C2-PFDA)	515.1 → 469.8	
	Sodium perfluoro-1-hexane[¹⁸ O ₂]sulfonate (18O2-PFHxS)	403.1 → 83.8	
	Sodium perfluoro-1-[1,2,3,4- ¹³ C ₄]octane sulfonate (13C4-PFOS)	502.9 → 79.9	

Table S6. Maximum, minimum, mean and median concentrations (ng/L) of PFASs at three drinking water intakes. *

	Community A				Community B				Community C			
	max	min	median	mean	max	min	median	mean	max	min	median	mean
PFBA	99	<10	26	33	38	<10	12	12	104	<10	12	22
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	36
PFHxA	318	<10	48	78	42	<10	<10	11	24	<10	<10	<10
PFHpA	324	<10	39	67	85	<10	<10	11	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	14	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	44	43	<25	<25	<25	40	<25	<25	<25
PFPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
PFOA+PFOS	447	0	64	90	59	0	0	9	55	<10	<10	<10
Σ PFASs**	1502	18	212	355	189	0	47	62	4696	55	345	710

* Concentrations less than quantitation limits were considered as zero to calculate means and Σ PFASs.

** Other PFECAs were present in water samples from community C but could not be quantified and were therefore not included in Σ PFASs

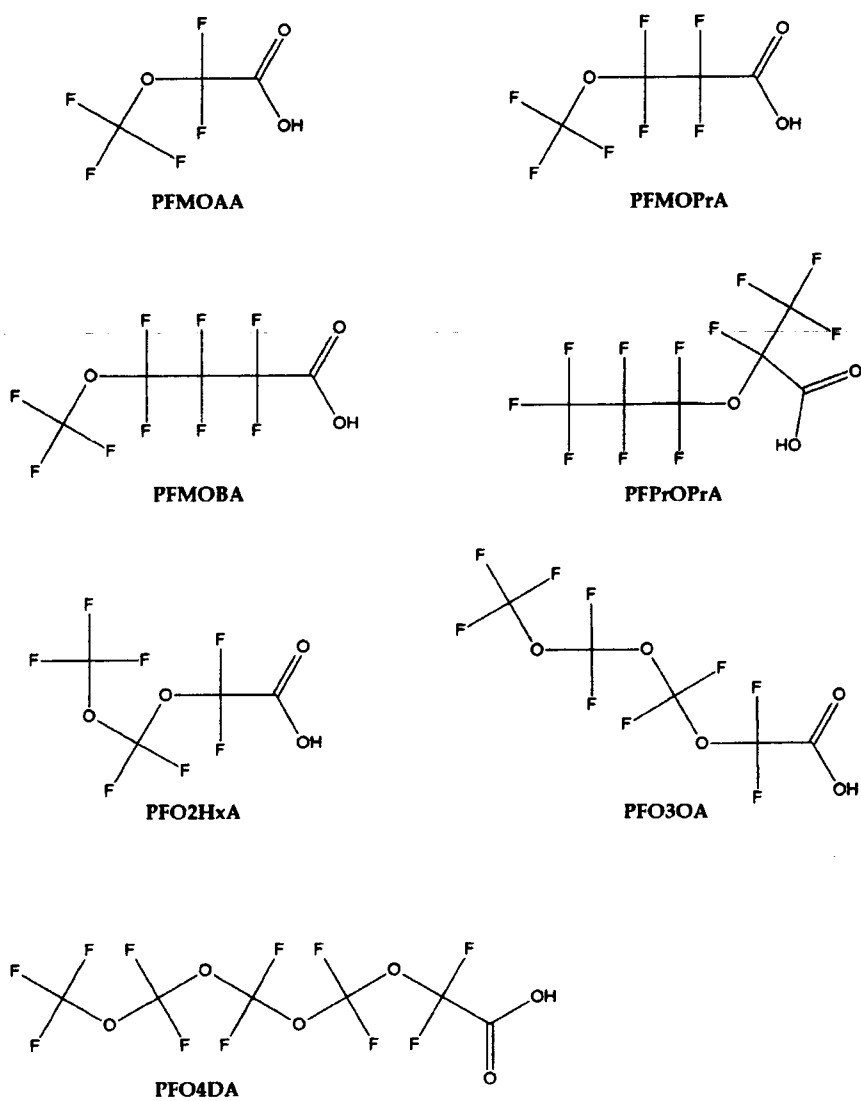


Figure S1. Molecular structures of PFECAs evaluated in this study

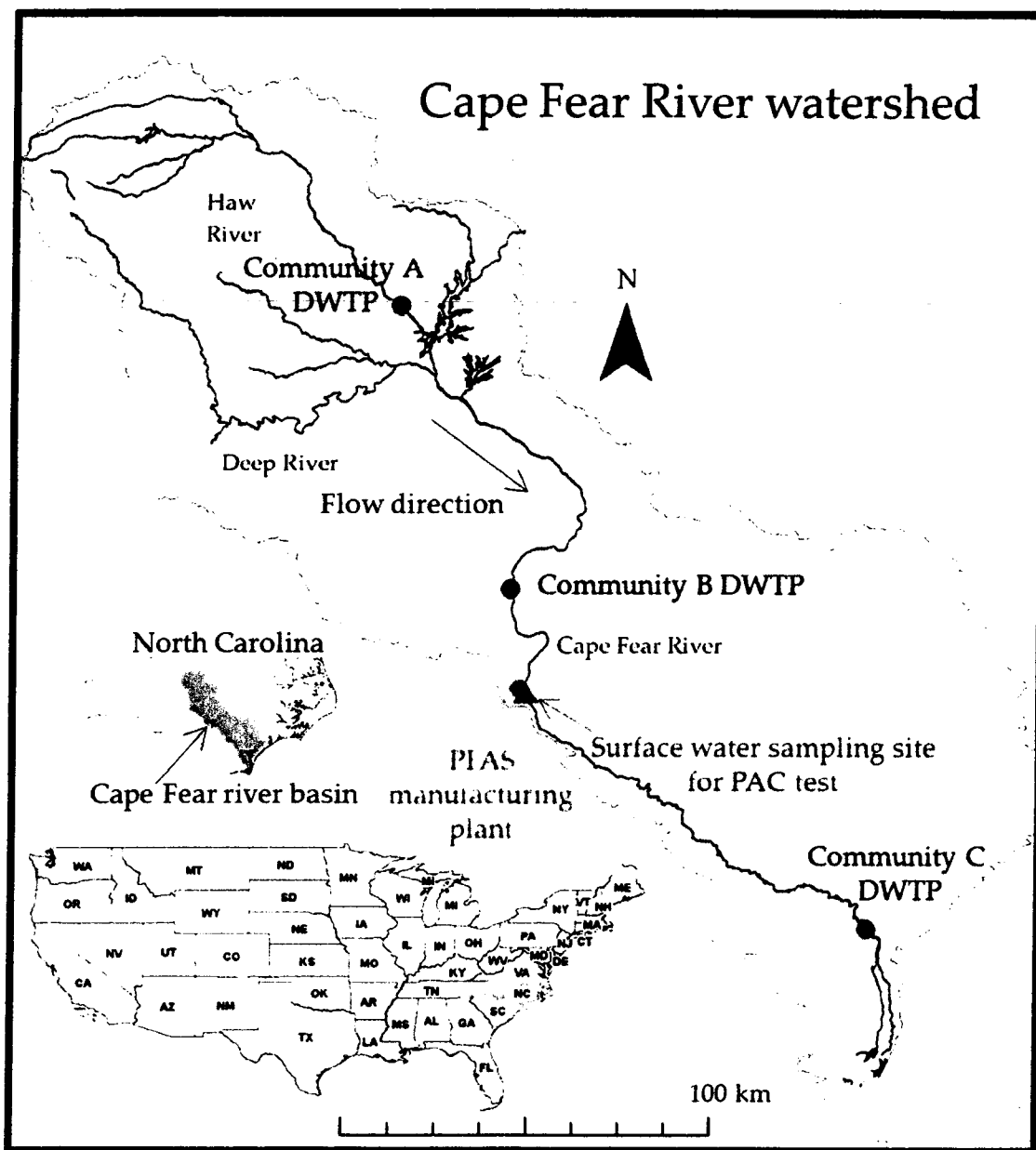
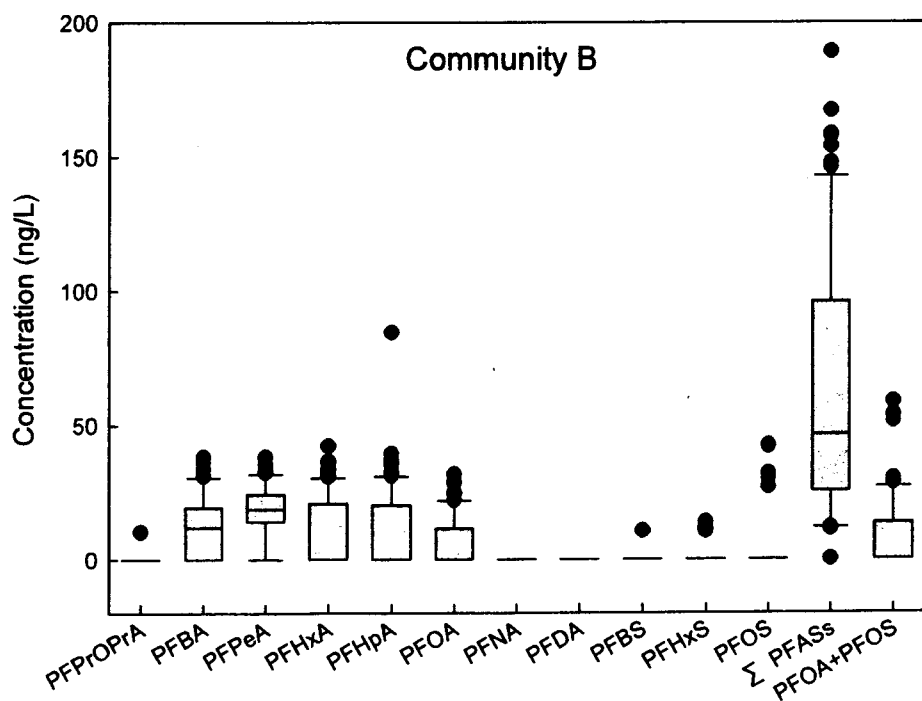
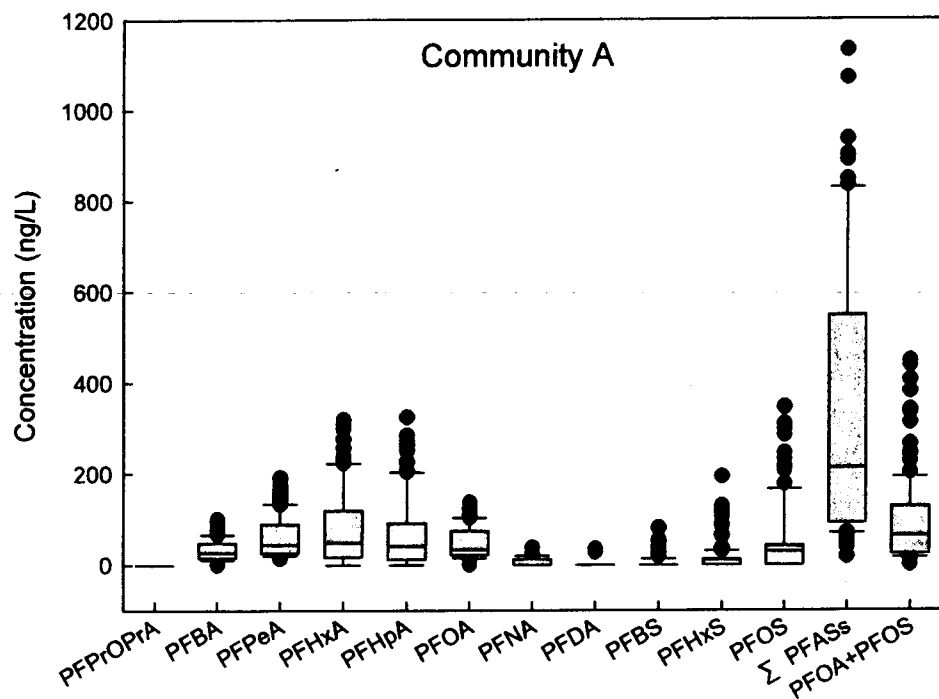


Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina. The scale is for the Cape Fear River watershed map.



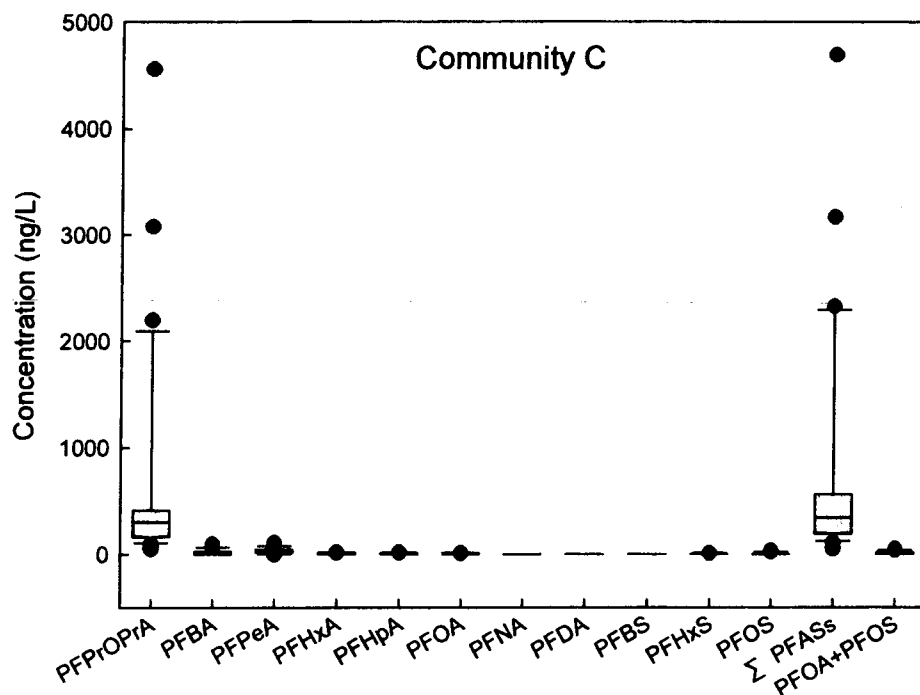


Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations less than quantitation limits were considered as zero. Upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; upper and lower bars represent the 90th and 10th percentile, respectively; and dots represent outliers (>90th or <10th percentile).

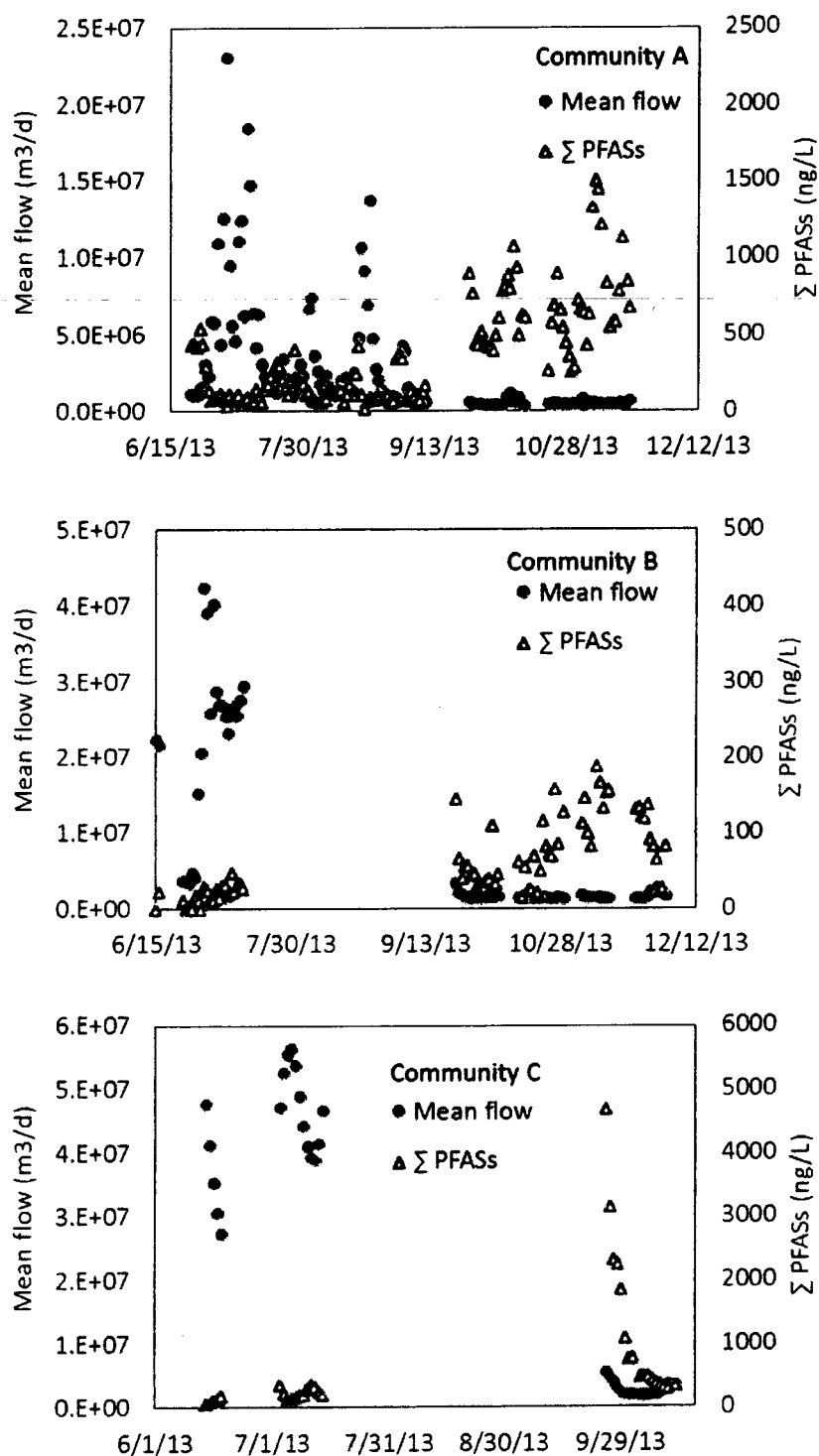


Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

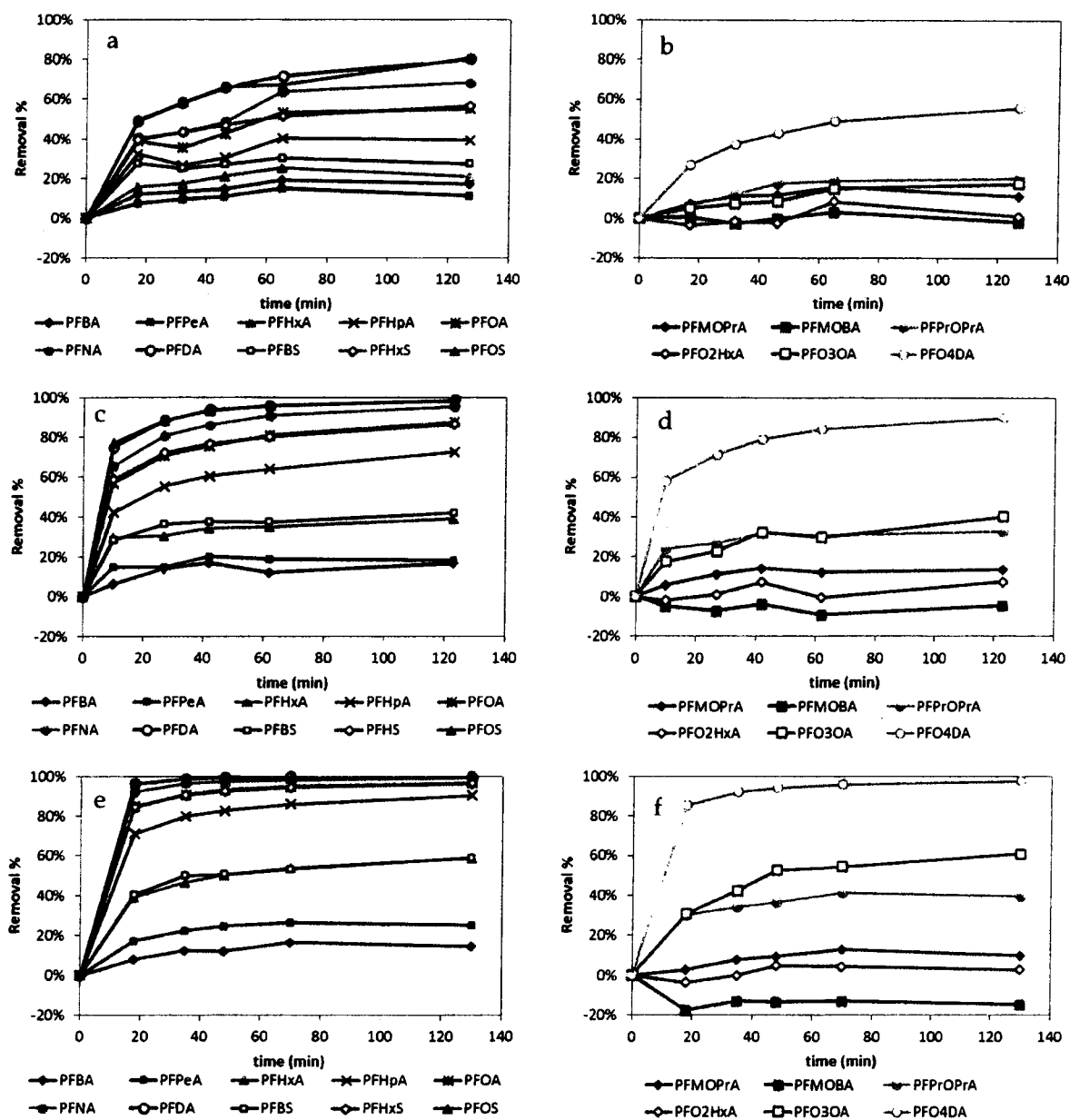


Figure S5. PFAS adsorption at powdered activated carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

Reference

1. Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B., Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environ. Sci. Technol.* **2007**, *41*, (15), 5271-5276.

Consent Orders

- **Chemical Name:** Azanium, 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate
- **Chemical Identifier:** 62037-80-3
- **Chemical Category:** Perfluoro Compounds; PBT chemicals;

[View Consent Orders](#)

What type of TSCA Section 5(e) Consent Order was developed for this chemical substance?:

Risk-based and Exposure-based Consent Order

Consent Order for: Azanium, 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate , 62037-80-3

Effective Date of TSCA Section 5(e) Consent Order: 1/28/2009

PMN Number: P-08-0509

Has the chemical been commenced?: Yes

Functional Use: Polymerization aid (generic)

What are the health or environmental toxicity concerns?:

- Aquatic and/or terrestrial toxicity:
- Cancer effects:
- Developmental/reproduction:
- Internal organs (e.g., liver, blood, kidney, etc.)/systemic toxicity:
- Lung toxicity (including lung overload):
- Mutagenicity:
- Persistent, Bioaccumulative, Toxic (PBT) properties:

What is the health or environmental concern based on?:

- Analog data:
- PBT chemicals:
- Perfluoro Compounds:
- Chemical testing:
- Physical/chemical properties:

Limitations on manufacture (including import), processing, distribution in commerce, use, or disposal pending submission and evaluation of information:

- As an alternative to using respirators, maintain workplace airborne concentrations of the PMN substance at or below a New Chemical Exposure Limit (NCEL): of 0.01 milligrams per cubic meter as an 8-hour time weighted average (TWA) verified by actual exposure monitoring:
- Disposal from manufacturing, processing, and/or use that differ from: the recovery and capture (destruction) or recycle of the PMN substance at an overall efficiency of 99% from all effluent streams and air emissions (point source and fugitive):
- Production volume greater than: the confidential aggregate manufacture volume identified in the consent order:
- Recordkeeping for all manufacturers and processors:

Has EPA modified or revoked the Consent Order based on submission of the listed testing?:

- No:

Consent Orders

- **Chemical Name:** 2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
- **Chemical Identifier:** 13252-13-6
- **Chemical Category:** Perfluoro Compounds; PBT chemicals;

[View Consent Orders](#)

What type of TSCA Section 5(e) Consent Order was developed for this chemical substance?:

Risk-based and Exposure-based Consent Order

Consent Order for: 2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid , 13252-13-6

Effective Date of TSCA Section 5(e) Consent Order: 1/28/2009

PMN Number: P-08-0508

Has the chemical been commenced?: Yes

Functional Use: Intermediate for polymerization aid (generic)

What are the health or environmental toxicity concerns?:

- Aquatic and/or terrestrial toxicity:
- Cancer effects:
- Developmental/reproduction:
- Internal organs (e.g., liver, blood, kidney, etc.)/systemic toxicity:
- Lung toxicity (including lung overload):
- Mutagenicity:
- Persistent, Bioaccumulative, Toxic (PBT) properties:

What is the health or environmental concern based on?:

- Analog data:
- PBT chemicals:
- Perfluoro Compounds:
- Chemical testing:
- Physical/chemical properties:

Limitations on manufacture (including import), processing, distribution in commerce, use, or disposal pending submission and evaluation of information:

- As an alternative to using respirators, maintain workplace airborne concentrations of the PMN substance at or below a New Chemical Exposure Limit (NCEL): of 0.01 milligrams per cubic meter as an 8-hour time weighted average (TWA) verified by actual exposure monitoring:
- Disposal from manufacturing, processing, and/or use that differ from: the recovery and capture (destruction) or recycle of the PMN substance at an overall efficiency of 99% from all effluent streams and air emissions (point source and fugitive):
- Production volume greater than: the confidential aggregate manufacture volume identified in the consent order:
- Recordkeeping for all manufacturers and processors:

Has EPA modified or revoked the Consent Order based on submission of the listed testing?:

- No:

North Carolina Department of Environmental Quality

Pat McCrory
Governor

Donald R. van der Vaart
Secretary

October 28, 2015

Mr. Michael Johnson, PE
Environmental Manager
The Chemours Company FC, LLC
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

Subject: NPDES Permit Modification
Permit NC0003573
Ownership Change
Bladen County
Class II Facility

Dear Mr. Johnson:

Division personnel have reviewed and approved your request for permit modification of the subject permit, to reflect new facility ownership effective July 1, 2015. Accordingly, we are enclosing modified pages to reflect the new ownership. Please insert these modified pages into your current permit. A complete review of this permit will be conducted with your next permit renewal in 2016. This permit modification is issued pursuant to the requirements of North Carolina General Statute 143-215.1 and the Memorandum of Agreement between North Carolina and the U.S. Environmental Protection Agency dated October 15, 2007 (or as subsequently amended). If you have any questions, feel free to contact me at 919-807-6390 or via email at tom.belnick@ncdenr.gov.

Sincerely,


S. Jay Zimmerman, P.G.
Director, Division of Water Resources

cc: NPDES Files
Central Files

Ecopy:
EPA Region 4
DWR Fayetteville Regional Office/Water Quality
DWR Aquatic Toxicology

1601 Mail Service Center, Raleigh, North Carolina 27699-1601
Phone: 919-707-8600 \ Internet: www.ncdenr.gov

DENR/DWQ
FACT SHEET FOR NPDES PERMIT DEVELOPMENT
 NPDES No. NC0003573

Facility Information			
Applicant/Facility Name:	E.I. DuPont de Nemours & Co – DuPont Fayetteville Works		
Applicant Address:	22828 NC Hwy 87W, Fayetteville, NC 28306-7332		
Facility Address:	22828 NC Hwy 87W, Fayetteville, NC 28306-7332		
Permitted Flow (MGD):	2 MGD – WWTP (Outfall 001 -external)		
Type of Waste:	Industrial		
Facility Classification:	III		
Permit Status:	Renewal		
County:	Bladen		
Miscellaneous			
Receiving Stream:	Cape Fear River	Regional Office:	Fayetteville
Stream Classification:	C, WS-IV	USGS Quad:	Duart
303(d) Listed?	No	Permit Writer:	Sergei Chernikov
Basin/Subbasin:	03-06-16	Date:	08/09/2011
Drainage Area (mi ²):	4790	 Lat. 34° 50' 18" N Long. 78° 49' 47" W	
Summer 7Q10 (cfs)	791		
Winter 7Q10 (cfs):			
30Q2 (cfs)			
Average Flow (cfs):	5676		
IWC (%):	3.3 %		

Summary:

E.I. DuPont de Nemours & Co submitted a permit renewal application on May 2, 2011 for the renewal of its NPDES permit. The DuPont Fayetteville Works manufacturing facility includes the Butacite® plant, the Nafion® plant, the Teflon® plant, and the APFO plant. A new process was added in 2011 to produce Polyvinyl Fluoride (PVF) resins. The process wastewaters generated from the new facility will be treated in the existing treatment plant.

Manufacturing Facilities:

Buticite® Manufacturing

- DuPont™ Buticite® Interlayer plastic sheeting – This is the final product used in safety glass such as automobile windshields.

Butacite® is manufactured in large rolls and shipped out in refrigerated trucks to glass manufacturers. The refrigeration is a requirement as butacite sticks to itself at temperatures above 60°F.

- Polyvinyl butyral (PVB) resin - the resin is shipped to other DuPont facilities for final processing.

Wastewaters generated at this facility are treated in the on-site wastewater treatment plant.

Nafion® Manufacturing

Five products are manufactured at the Nafion® manufacturing facility:

- DuPont™ Nafion® membrane – a plastic film used in the chloroalkali industry and in electrochemical fuel cells;

- Nafion® resins – ultimately extruded into a finished film;
- Nafion® solution – generated during the production of resin;
- FLPR vinyl ether monomers – shipped to other DuPont locations to produce various fluorochemical products such as DuPont™ Teflon®.
- HFPO monomers – shipped to other DuPont locations to produce various fluorochemical products such as DuPont™ Teflon®.

Wastewaters generated at this facility are neutralized and treated in the on-site WWTP.

PPA Manufacturing

The processing aids produced in this units are used to produce fluoropolymers and fluorinated telomers that are shipped to other DuPont facilities. This facility was started up in November 2002.

Wastewaters generated in this process are collected and shipped off-site for disposal.

Sentry Glass Plus® Manufacturing

DuPont™ Sentry Glass Plus® - this is an ionoplast interlayer laminate used for laminated safety glass in side, rear, and overhead automobile windows. It is also used in architectural applications desiring safety glass.

This manufacturing process started in June 2005. No process wastewaters are generated from this process. Non-contact cooling water is discharged to Outfall 002.

Proposed PVF-3 Manufacturing

This facility will produce Poliviny fluoride resins (PVF) and is expected to start production in 2013. The manufacturing facility will be located near the existing PVF-1 and PVF-2 manufacturing processes. PVF is used in DuPont™ Tedlar® fluoropolymer film manufactured at other DuPont facilities. Tedlar® is used in the photovoltaic industry in photovoltaic cells and the aircraft industry for interior cabin surfaces, as well as other uses.

The PVF-1 facility began operation during September 2007, the PVF-2 facility began operation during June 2010. Process wastewater generated from this manufacturing facility is treated in the WWTP. Non-contact cooling water, condensate and stormwater will be discharged to Outfall 002.

Wastewater Treatment:

Process wastewaters and stormwater from process areas are collected in sumps in the respective manufacturing areas and conveyed via gravity sewers to the wastewater treatment plant. Sanitary sewage is conveyed separately to the WWTP.

The treatment system discharges through Outfall 001 to the main discharge channel. Non-process cooling waters and stormwater are conveyed to ditches and discharged to the main discharge channel. The combined flows are discharged through Outfall 002 to the Cape Fear River below Lock and Dam #3.

Effluent Guidelines:

DuPont's Fayetteville Works is regulated under the Organic Chemicals, Plastics and Synthetic Fibers Category, 40 CFR 414 Subpart D. These guidelines apply to products manufactured under SIC codes 2869 and 2821. SIC code 2869 includes Nafion® solution, Vinyl Ether and HFPO monomers manufacturing. SIC code 2821 includes Teflon® resin, polyvinyl fluoride resin, polyvinyl butyral resin and Nafion® resin manufacturing. Manufacturing of Nafion membrane, Butacite® sheeting and Sentry Glass plus are classified as SIC code 3081 which is not regulated by the OCPSF guidelines.

Regulated process flow for Outfall 001 is approximately 0.9 MGD. This flow includes the flow from PVF manufacturing process.

EG limits - Subpart D - Thermoplastic Resins, 414.41

Limits are calculated by multiplying the allocation from the effluent guidelines by 8.34 (conversion factor) and by OCPSF process flow.

Parameter	Effluent Limitations (concentration)		Effluent Limitations (Mass limits)		Domestic WW (mass limits)		Proposed limits (mass limits)	
	Maximum Daily (mg/l)	Maximum Monthly Average (mg/l)	Daily Maximum (lb/day)	Monthly Average (lb/day)	Daily Maximum (lb/day)	Monthly Average (lb/day)	Daily Maximum (lb/day)	Monthly Average (lb/day)
BOD	64	24	481.7	180.6	3	2	484.7	182.6
TSS	130	40	978.5	301.1	3	2	981.5	303.1

Process flow - 0.9025 MGD.

Compliance Summary:

During the review period (2007-2011) the facility did not receive any Notices of Violation.

Whole Effluent Toxicity - The permit requires a quarterly chronic test at 3.3 %. The facility passed all the tests during the previous permit term (please see attached).

Reasonable Potential Analysis (RPA):

The RPA was conducted for F, please see attached.

Instream data review:

There are monitoring stations in the Cape Fear River upstream (B8301000) and downstream (B8302000) of the discharge. Data from the monitoring stations indicates no noticeable impact from the discharge.

SUMMARY OF PROPOSED CHANGES:

- One clarifier was added to the description of the treatment facility.
- The permit limits have recalculated based on the latest OCPSF production information in accordance with the 40 CFR 414 Subpart D.
- The limits for Cr, Cu, CN, Pb, Ni, and Zn were added to the permit in accordance with the 40 CFR 414 Subpart D.
- The limit for F was removed from the permit based on the statistical analysis of the effluent data and the monitoring was reduced to quarterly. The instream monitoring for F was removed from the permit.

PROPOSED SCHEDULE FOR PERMIT ISSUANCE

Draft Permit to Public Notice:

August 31, 2011

Permit Scheduled to Issue:

October 24, 2011

NPDES DIVISION CONTACT

If you have questions regarding any of the above information or on the attached permit, please contact Sergei Chernikov at (919) 807-6393.

CHANGES IN THE FINAL PERMIT:

- Tertiary filters were removed from the description of the wastewater treatment facilities.
- Classification of the receiving stream was changes to Class C, WS-IV.
- Cooling tower blowdown was added to the description of waste streams.
- Chronic toxicity monitoring requirement was moved to the Outfall 002.

North Carolina Department of Environmental Quality

Pat McCrory
Governor

Donald R. van der Vaart
Secretary

October 28, 2015

Mr. Michael Johnson, PE
Environmental Manager
The Chemours Company FC, LLC
22828 NC Highway 87 W
Fayetteville, NC 28306-7332

Subject: NPDES Permit Modification
Permit NC0003573
Ownership Change
Bladen County
Class II Facility

Dear Mr. Johnson:

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Sincerely,



SJZ S. Jay Zimmerman, P.G.
Director, Division of Water Resources

cc: NPDES Files
Central Files

Ecopy:
EPA Region 4
DWR Fayetteville Regional Office/Water Quality
DWR Aquatic Toxicology

1601 Mail Service Center, Raleigh, North Carolina 27699-1601
Phone: 919-707-8600 \ Internet: www.ncdenr.gov

**STATE OF NORTH CAROLINA
DEPARTMENT OF ENVIRONMENTAL QUALITY
DIVISION OF WATER RESOURCES**

NPDES PERMIT

**TO DISCHARGE WASTEWATER UNDER THE
NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM**

In compliance with the provisions of North Carolina General Statute 143-215.1, other lawful standards and regulations promulgated and adopted by the North Carolina Environmental Management Commission, and the Federal Water Pollution Control Act, as amended,

The Chemours Company FC, LLC

is hereby authorized to discharge wastewater and stormwater from a facility located at

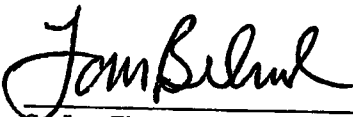
**Chemours Company- Fayetteville Works
22828 NC Highway 87 W
Fayetteville
Bladen County**

to receiving waters designated as the Cape Fear River in the Cape Fear River Basin in accordance with effluent limitations, monitoring requirements, and other conditions set forth in Parts I, II, III, and IV hereof.

The permit modification shall become effective July 1, 2015.

This permit and the authorization to discharge shall expire at midnight on October 31, 2016.

Signed this day October 28, 2015.


S. Jay Zimmerman, P.G.
Director, Division of Water Resources
By Authority of the Environmental Management Commission

SUPPLEMENT TO PERMIT COVER SHEET

All previous NPDES Permits issued to this facility, whether for operation or discharge are hereby revoked, and as of this issuance, any previously issued permit bearing this number is no longer effective. Therefore, the exclusive authority to operate and discharge from this facility arises under the permit conditions, requirements, terms, and provisions included herein.

The Chemours Company FC, LLC

is hereby authorized to:

1. Continue to operate existing wastewater treatment facilities consisting of:
 - equalization;
 - neutralization;
 - aerated pre-digester tank;
 - nutrient feed system;
 - aeration tank;
 - three clarifiers;
 - effluent flow measurement;
 - DAF unit;
 - rotary filter for sludge thickening;
 - sludge pump;
 - sludge filter press; and
 - steam heated sludge dryers.
2. Discharge treated process wastewater from Butacite®, Nafion®, SentryGlas®, and PVF (polyvinyl fluoride resin), process stormwater, sanitary wastewater, and co-neutralized regenerate from said treated facilities through internal outfall 001;
3. Discharge stormwater, non-contact cooling water, boiler blowdown and condensate, cooling tower blowdown, and treated wastewater effluent from 001, through outfall 002 at the location specified on the attached map into the Cape Fear River, a class C, WS-IV water in the Cape Fear River Basin.

**STATE OF NORTH CAROLINA
DEPARTMENT OF ENVIRONMENTAL QUALITY
DIVISION OF WATER RESOURCES**

NPDES PERMIT

**TO DISCHARGE WASTEWATER UNDER THE
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**Chemours Company- Fayetteville Works
22828 NC Highway 87 W
Fayetteville
Bladen County**

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3. Discharge stormwater, non-contact cooling water, boiler blowdown and condensate, cooling tower blowdown, and treated wastewater effluent from 001, through outfall 002 at the location specified on the attached map into the Cape Fear River, a class C, WS-IV water in the Cape Fear River Basin.

A. (1) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee is authorized to discharge from **Outfall 001**. Such discharges shall be limited and monitored by the Permittee as specified below:

PARAMETER	EFFLUENT LIMITATIONS		MONITORING REQUIREMENTS		
	Monthly Average	Daily Maximum	Measurement Frequency	Sample Type	Sample Location
Flow (MGD)	2.0		Continuous	Recording	Effluent
BOD ₅ , 20° C	182.6 lbs/day	484.7 lbs/day	3/Week	Composite	Effluent
Total Suspended Solids	303.1 lbs/day	981.5 lbs/day	3/Week	Composite	Effluent
Temperature			Weekly	Grab	Effluent
Oil & Grease			Monthly	Grab	Effluent
pH	Between 6.0 and 9.0 Standard Units		3/Week	Grab	Effluent
40 CFR 414 Subpart I	See Condition A. (2)				

THERE SHALL BE NO DISCHARGE OF FLOATING SOLIDS OR VISIBLE FOAM IN OTHER THAN TRACE AMOUNTS.

A. (2) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS - SUBPART I

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee shall comply with the limitations and monitoring frequencies established below at outfall 001:

PARAMETER	EFFLUENT LIMITATIONS	MONITORING REQUIREMENTS
-----------	----------------------	-------------------------

	Monthly Average ¹	Daily Maximum ¹	Measurement Frequency	Sample Type	Sample Location
Acenaphthene	0.166	0.444	See Note 2	Grab	Effluent
Acenaphthylene	0.166	0.444	See Note 2	Grab	Effluent
Acrylonitrile	0.723	1.821	See Note 2	Grab	Effluent
Anthracene	0.166	12.8 ug/L	See Note 2	Grab	Effluent
Benzene	0.278	1.024	See Note 2	Grab	Effluent
Benzo(a)anthracene	0.166	0.444	See Note 2	Grab	Effluent
3,4-Benzofluoranthene	0.173	0.459	See Note 2	Grab	Effluent
Benzo(k)fluoranthene	0.166	0.444	See Note 2	Grab	Effluent
Benzo(a)pyrene	0.173	0.459	See Note 2	Grab	Effluent
Bis(2-ethylhexyl) phthalate	0.775	2.100	See Note 2	Grab	Effluent
Carbon Tetrachloride	0.135	0.286	See Note 2	Grab	Effluent
Chlorobenzene	0.113	0.211	See Note 2	Grab	Effluent
Chloroethane	0.783	2.017	See Note 2	Grab	Effluent
Chloroform	0.158	0.346	See Note 2	Grab	Effluent
2-Chlorophenol	0.233	0.738	See Note 2	Grab	Effluent
Chrysene	0.166	0.444	See Note 2	Grab	Effluent
Di-n-butyl phthalate	0.203	0.429	See Note 2	Grab	Effluent
1,2-Dichlorobenzene	0.580	1.227	See Note 2	Grab	Effluent
1,3-Dichlorobenzene	0.233	0.331	See Note 2	Grab	Effluent
1,4-Dichlorobenzene	0.113	0.211	See Note 2	Grab	Effluent
1,1-Dichloroethane	0.166	0.444	See Note 2	Grab	Effluent
1,2-Dichloroethane	0.512	1.588	See Note 2	Grab	Effluent
1,1-Dichloroethylene	0.120	0.188	See Note 2	Grab	Effluent
1,2-trans-Dichloroethylene	0.158	0.406	See Note 2	Grab	Effluent
2,4-Dichlorophenol	0.294	0.843	See Note 2	Grab	Effluent
1,2-Dichloropropane	1.152	1.731	See Note 2	Grab	Effluent
1,3-Dichloropropylene	0.218	0.331	See Note 2	Grab	Effluent
Diethyl phthalate	0.610	1.528	See Note 2	Grab	Effluent
2,4-Dimethylphenol	0.135	0.271	See Note 2	Grab	Effluent
Dimethyl phthalate	0.143	0.354	See Note 2	Grab	Effluent
4,6-Dinitro-o-cresol	0.587	2.085	See Note 2	Grab	Effluent
2,4-Dinitrophenol	0.534	0.926	See Note 2	Grab	Effluent
2,4-Dinitrotoluene	0.851	2.145	See Note 2	Grab	Effluent
2,6-Dinitrotoluene	1.919	12.3 ug/L	See Note 2	Grab	Effluent
Ethylbenzene	0.241	0.813	See Note 2	Grab	Effluent

A. (2) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS - SUBPART I (CONTUNUED)

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee shall comply with the limitations and monitoring frequencies established below at outfall 001:

PARAMETER	EFFLUENT LIMITATIONS	MONITORING REQUIREMENTS
-----------	----------------------	-------------------------

	Monthly Average ¹	Daily Maximum ¹	Measurement Frequency	Sample Type	Sample Location
Fluoranthene	0.188	28.2 ug/L	See Note 2	Grab	Effluent
Fluorene	0.166	0.444	See Note 2	Grab	Effluent
Hexachlorobenzene	0.113	0.5 µg/L	Annually ³	Grab	Effluent
Hexachlorobutadiene	0.151	0.369	See Note 2	Grab	Effluent
Hexachloroethane	0.158	0.406	See Note 2	Grab	Effluent
Methyl Chloride	0.647	1.430	See Note 2	Grab	Effluent
Methylene Chloride	0.301	0.670	See Note 2	Grab	Effluent
Naphthalene	0.166	0.444	See Note 2	Grab	Effluent
Nitrobenzene	0.203	0.512	See Note 2	Grab	Effluent
2-Nitrophenol	0.309	0.519	See Note 2	Grab	Effluent
4-Nitrophenol	0.542	0.933	See Note 2	Grab	Effluent
Phenanthrene	0.166	0.444	See Note 2	Grab	Effluent
Phenol	0.113	0.196	See Note 2	Grab	Effluent
Pyrene	0.188	0.504	See Note 2	Grab	Effluent
Tetrachloroethylene	0.166	0.422	See Note 2	Grab	Effluent
Toluene	0.196	0.602	See Note 2	Grab	Effluent
1,2,4-Trichlorobenzene	0.512	1.054	See Note 2	Grab	Effluent
1,1,1-Trichloroethane	0.158	0.406	See Note 2	Grab	Effluent
1,1,2-Trichloroethane	0.158	0.406	See Note 2	Grab	Effluent
Trichloroethylene	0.158	0.406	See Note 2	Grab	Effluent
Vinyl Chloride	0.783	2.017	See Note 2	Grab	Effluent
Total Chromium	8.355	20.849	Annually	Grab	Effluent
Total Copper	10.914	25.441	Annually	Grab	Effluent
Total Cyanide	3.161	9.032	See Note 2	Grab	Effluent
Total Lead	2.409	5.194	See Note 2	Grab	Effluent
Total Nickel	12.720	29.957	Annually	Grab	Effluent
Total Zinc	7.903	19.645	Annually	Grab	Effluent

Notes:

1. All units are lbs/day unless otherwise noted.
2. Monitoring for the specified parameters has been waived based on a demonstration made by the Permittee in accordance with 40 CFR 122.44(a)(2)(i). This waiver is good only for the term of the permit. Please note that any exceedence of the effluent limitations found herein shall be considered a permit violation subject to appropriate enforcement action.
3. The most sensitive analytical method available shall be employed for determining the presence of hexachlorobenzene in the effluent.

A. (3) EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

Beginning on the effective date of this permit and lasting through the expiration date, the Permittee is authorized to discharge from **Outfall 002 (boiler blowdown, once-through cooling water, and treated wastewater from outfall 001)** Such discharges shall be limited and monitored by the Permittee as specified below:

PARAMETER	EFFLUENT LIMITATIONS		MONITORING REQUIREMENTS		
	Monthly Average	Daily Maximum	Measurement Frequency	Sample Type	Sample Location ¹
Flow (MGD)			Continuous	Recording	Effluent or Influent
Temperature, °C	See Note 2		Daily ³	Grab	Effluent, Upstream, Downstream
BOD ₅ , 20°C			Quarterly	Composite	Effluent
COD			Quarterly	Composite	Effluent
Fluoride (ug/L)			Quarterly	Grab	Effluent
Dissolved Oxygen			Weekly	Grab	Upstream, Downstream
PFOA ⁴			Monthly	Grab	Effluent
Total Phosphorus			Monthly	Composite	Effluent
Total Nitrogen (NO ₂ +NO ₃ +TKN)			Monthly	Composite	Effluent
Conductivity			Weekly	Grab	Upstream, Downstream
Chronic Toxicity	See Note 5		Quarterly	Composite	Effluent
pH	Between 6.0 and 9.0 Standard Units		3/Week	Grab	Effluent

Notes:

- Upstream shall be at the Permittee's river pump station; downstream shall be at the boat ramp approximately 4500 feet downstream at Prospect Hall Landing.
As a participant in the Middle Cape Fear River Basin Association, the instream monitoring requirements as stated above are waived. Should your membership in the agreement be terminated, you shall notify the Division immediately and the instream monitoring requirements specified in your permit shall be reinstated.
- The temperature of the effluent shall be such as not to cause an increase in the temperature of the receiving stream of more than 2.8°C and in no case cause the ambient water temperature to exceed 32°C.
- Daily shall be defined as every day except Saturdays, Sundays, and legal holidays. Instream temperature sampling shall be conducted weekly.
- PFOA (Perfluorooctanoic acid) - The Cape Fear River water intake may be sampled for PFOA on a monthly basis and reported as an upstream parameter in DWQ Form - MR-3.
- Chronic Toxicity (*Ceriodaphnia*) P/F @ 3.3% February, May, August, November; see condition A. (4) of this permit. The compliance monitoring point for chronic toxicity shall be downstream of the confluence of outfall 001 and 002.

THERE SHALL BE NO DISCHARGE OF FLOATING SOLIDS OR VISIBLE FOAM IN OTHER THAN TRACE AMOUNTS.

A. (4) CHRONIC TOXICITY PERMIT LIMIT (QUARTERLY) - OUTFALL 002

The effluent discharge shall at no time exhibit observable inhibition of reproduction or significant mortality to *Ceriodaphnia dubia* at an effluent concentration of 3.3%.

The permit holder shall perform at a minimum, quarterly monitoring using test procedures outlined in the "North Carolina *Ceriodaphnia* Chronic Effluent Bioassay Procedure," Revised February 1998, or subsequent versions or "North Carolina Phase II Chronic Whole Effluent Toxicity Test Procedure" (Revised-February 1998) or subsequent versions. The tests will be performed during the months of February, May, August, and November. Effluent sampling for this testing shall be performed at the NPDES permitted final effluent discharge below all treatment processes.

If the test procedure performed as the first test of any single quarter results in a failure or ChV below the permit limit, then multiple-concentration testing shall be performed at a minimum, in each of the two following months as described in "North Carolina Phase II Chronic Whole Effluent Toxicity Test Procedure" (Revised-February 1998) or subsequent versions.

The chronic value for multiple concentration tests will be determined using the geometric mean of the highest concentration having no detectable impairment of reproduction or survival and the lowest concentration that does have a detectable impairment of reproduction or survival. The definition of "detectable impairment," collection methods, exposure regimes, and further statistical methods are specified in the "North Carolina Phase II Chronic Whole Effluent Toxicity Test Procedure" (Revised-February 1998) or subsequent versions.

All toxicity testing results required as part of this permit condition will be entered on the Effluent Discharge Monitoring Form (MR-1) for the months in which tests were performed, using the parameter code TGP3B for the pass/fail results and THP3B for the Chronic Value. Additionally, DWQ Form AT-3 (original) is to be sent to the following address:

Attention: Environmental Sciences Section
North Carolina Division of Water Quality
1621 Mail Service Center
Raleigh, North Carolina 27699-1621

Completed Aquatic Toxicity Test Forms shall be filed with the Environmental Sciences Section no later than 30 days after the end of the reporting period for which the report is made.

Test data shall be complete, accurate, include all supporting chemical/physical measurements and all concentration/response data, and be certified by laboratory supervisor and ORC or approved designate signature. Total residual chlorine of the effluent toxicity sample must be measured and reported if chlorine is employed for disinfection of the waste stream.

Should there be no discharge of flow from the facility during a month in which toxicity monitoring is required, the permittee will complete the information located at the top of the aquatic toxicity (AT) test form indicating the facility name, permit number, pipe number, county, and the month/year of the report with the notation of "No Flow" in the comment area of the form. The report shall be submitted to the Environmental Sciences Section at the address cited above.

Should the permittee fail to monitor during a month in which toxicity monitoring is required, monitoring will be required during the following month.

Should any test data from this monitoring requirement or tests performed by the North Carolina Division of Water Quality indicate potential impacts to the receiving stream, this permit may be re-opened and modified to include alternate monitoring requirements or limits.

NOTE: Failure to achieve test conditions as specified in the cited document, such as minimum control organism survival, minimum control organism reproduction, and appropriate environmental controls, shall constitute an invalid test and will require immediate follow-up testing to be completed no later than the last day of the month following the month of the initial monitoring.

A. (5) RE-OPENER CONDITION

This permit shall be modified, or revoked and reissued to incorporate additional toxicity limitations and monitoring requirements in the event toxicity testing or other studies conducted on the effluent or receiving stream indicate that detrimental effects may be expected in the receiving stream as a result of this discharge.

A. (6) BIOCIDES CONDITION

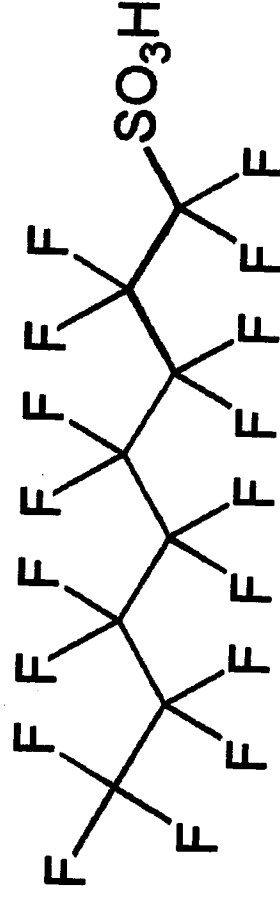
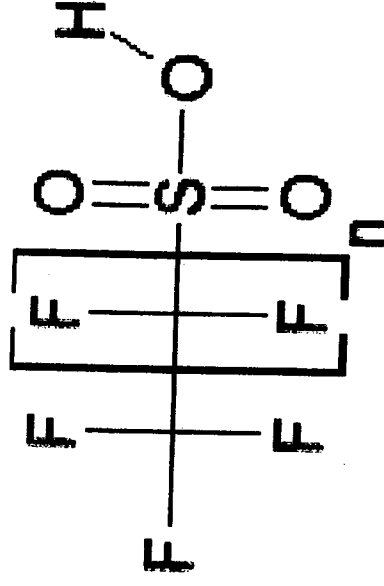
The permittee shall not use any biocide except those approved in conjunction with the permit application. The permittee shall notify the Director in writing not later than ninety (90) days prior to instituting use of any additional biocide used in cooling systems which may be toxic to aquatic life other than those previously reported to the Division of Water Quality. Such notification shall include completion of Biocide Worksheet Form 101 and a map locating the discharge point and receiving stream.

Perfluoroalkyl ether carboxylic acids: Occurrence in the Cape Fear river watershed and fate in drinking water treatment processes

**Mei Sun, Elisa Arevalo, Leigh-Ann Dudley,
Andrew Lindstrom, Mark Strynar, Detlef Knappe**



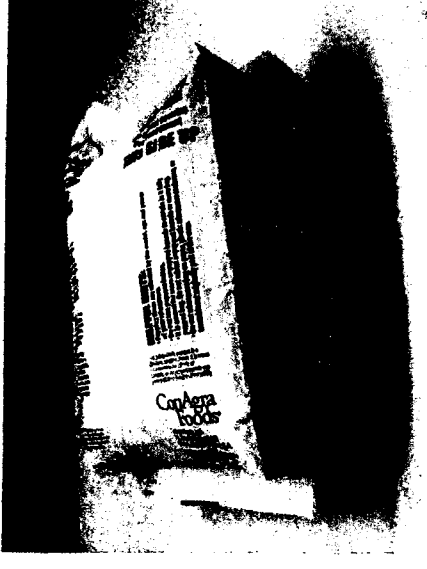
THE UNIVERSITY OF CHICAGO



Long-chain PFASs have long half-lives in humans

- Half-lives in humans

- PFOA: 3.8 years
- PFOS: 5.4 years
- PFBS: 4 months

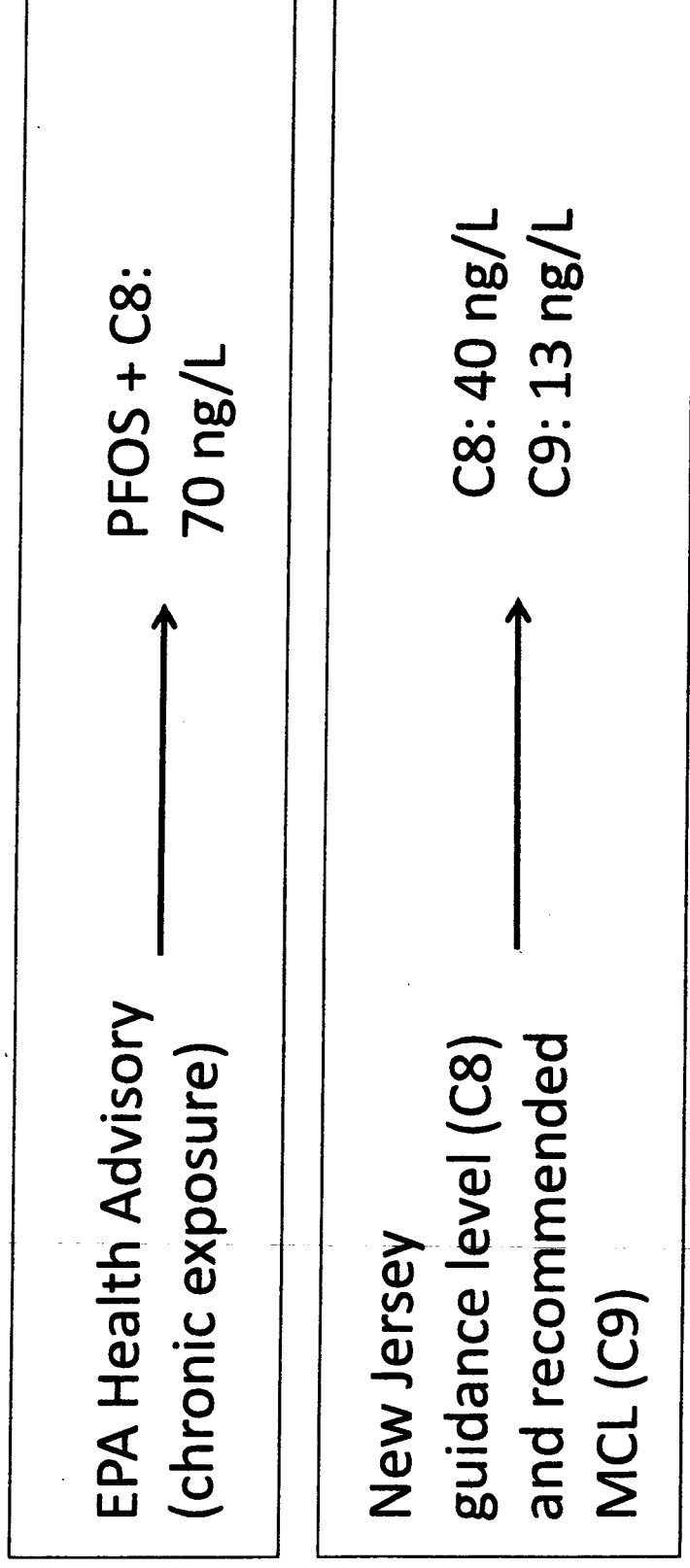


- Toxicokinetic differences for PFOA

- 17-19 days in mice
- 4 hours in female rats




To protect the public from adverse health effects, health based guidelines have been established



Are PFASs a concern in US drinking water?

Six PFASs were included in the third Unregulated Contaminant Monitoring Rule (UCMR3)

Compound	MRL (ng/L)
Perfluoroheptanoic acid (PFHpA, C7)	10
Perfluorooctanoic acid (PFOA, C8)	20
Perfluorononanoic acid (PFNA, C9)	20
Perfluorobutanesulfonic acid (PFBS)	90
Perfluorohexanesulfonic acid (PFHxS)	30
Perfluorooctanesulfonic acid (PFOS)	40



Samples collected from January 2013 – December 2015
Public Water Systems (PWSs) serving >10,000 people

At first glance, UCMR3 data suggest low PFAS detection frequency

UCMR3 requires monitoring for six PFASs in US drinking water. Monitoring began in 2013, and latest data release was January 2017.

PFAS	MRL (ng/L)	Occurrence (%)	Max. Concentration (ng/L)	Locations with high concentrations
C7	10	0.64	410	Saipan, PA, NY, DE, CO
C8	20	1.03	349	PA, MN, Saipan, DE, WV
C9	20	0.05	56	NJ, DE, PA, MA, NY
PFBS	90	0.05	370	GA, Saipan, CO, AL, PA
PFHxS	30	0.56	1,600	Saipan, AZ, DE, CO, PA
PFOS	40	0.79	7,000	Saipan, DE, CO, PA, WA

36,972 samples from 4,920 PWSs

PFAS detects: 599 samples (1.6%) from 198 PWSs (4.0%)

Of samples with PFAS detects: 23.4% derived from surface water

Some drinking water samples had PFOA+PFOS levels well above the HAL

UCMR3 Data for North Carolina: PFAS detection frequency higher than for entire US

Compound	MRL (ng/L)	NC Detects
Perfluoroheptanoic acid (PFHpA, C7)	10	29 (max. 60 ng/L)
Perfluorooctanoic acid (PFOA, C8)	20	10 (max. 30 ng/L)
Perfluorononanoic acid (PFNA, C9)	20	0
Perfluorobutanesulfonic acid (PFBS)	90	0
Perfluorohexanesulfonic acid (PFHxS)	30	5 (max. 110 ng/L)
Perfluorooctanesulfonic acid (PFOS)	40	8 (max. 90 ng/L)

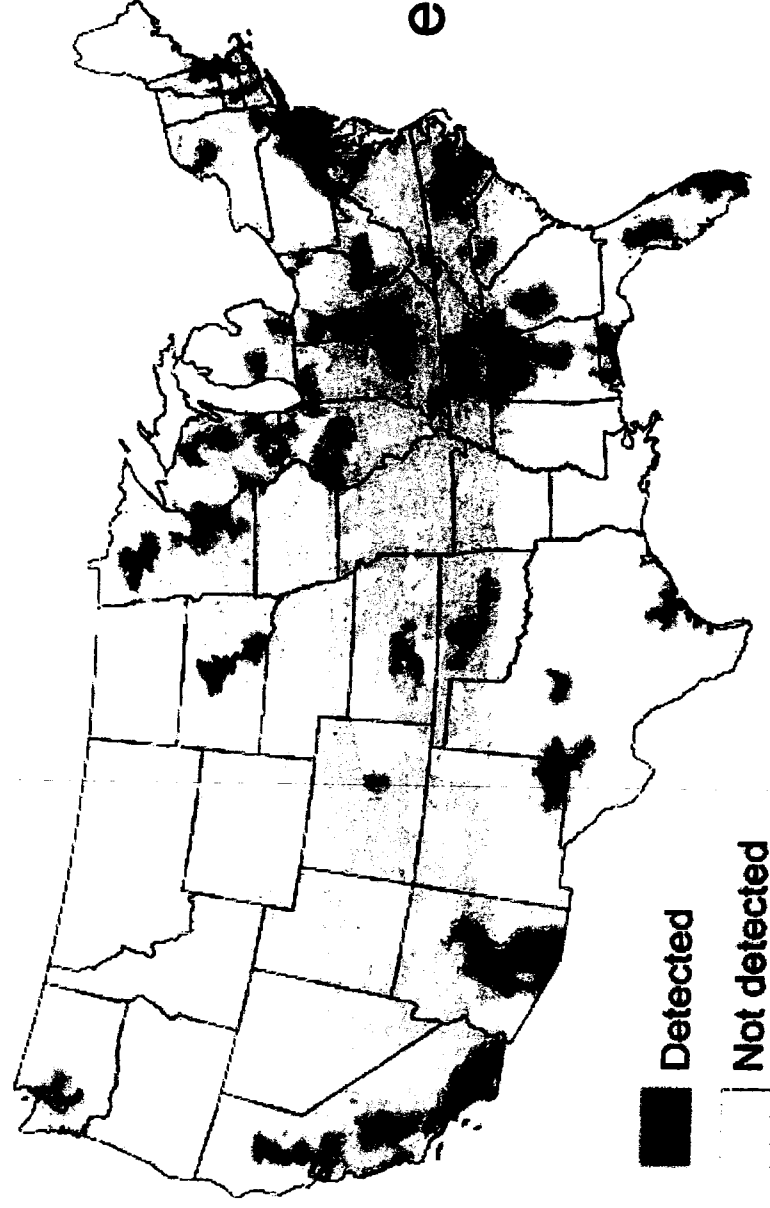
1,320 samples from 151 PWSs in NC

PFAS detects: 43 samples (3.3%) from 20 PWSs (13.2%)

Of samples with PFAS detects: 79% derived from surface water

Elevated PFAS levels affect a sizeable number of US residents

Hydrological units with detectable PFASs



PFOS+PFOA levels estimated to exceed the 70 ng/L HAL in the drinking water of 6 million US residents

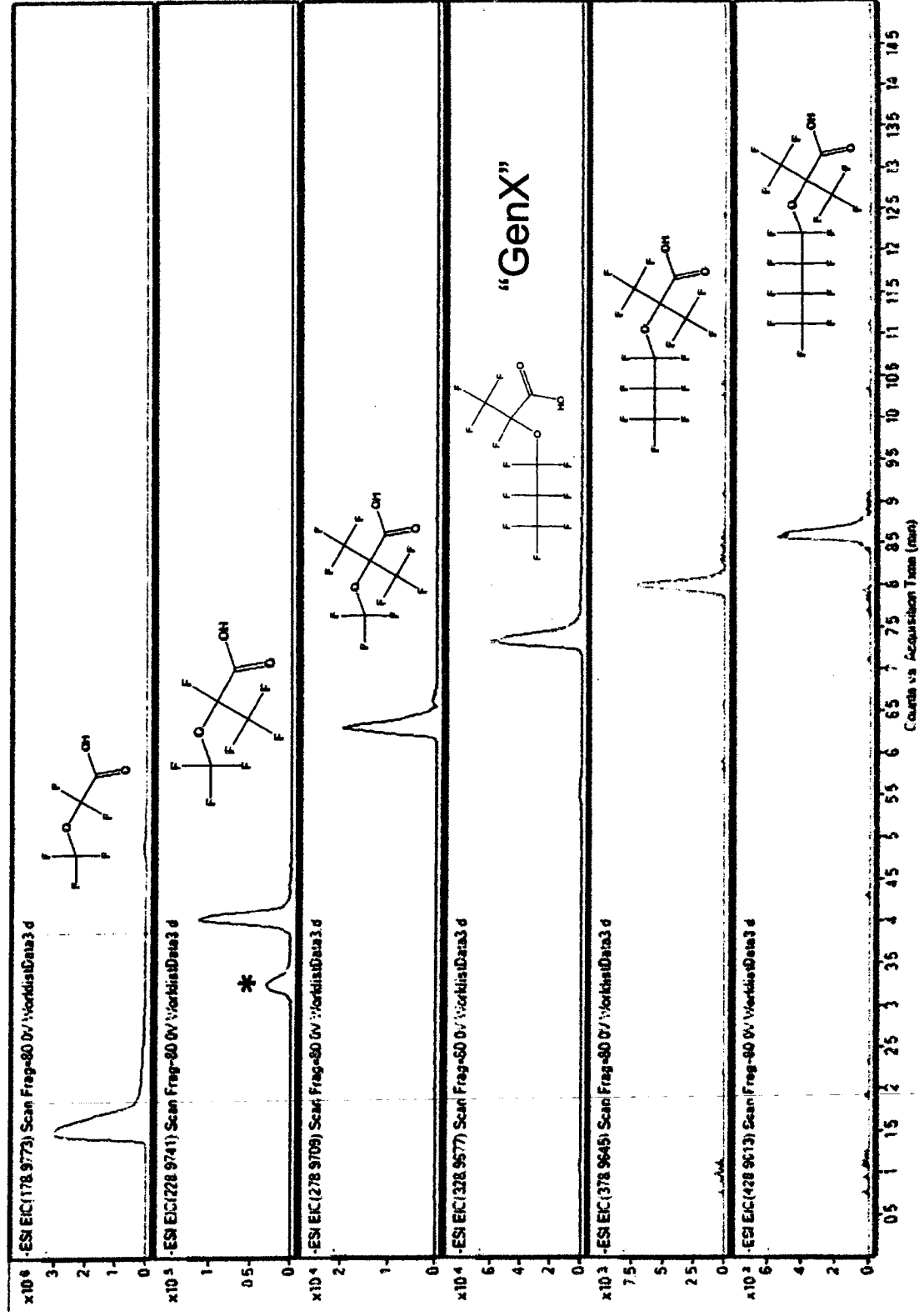
**...but are we
seeing the
complete picture?**

Many PFASs are used in commerce

Sub-classes of PFASs	Examples of Individual compounds*	Number of peer-reviewed articles since 2002**
perfluoroalkyl acids (PFAAs)	PFCAs $(C_nF_{2n+1}-COOH)$	PFBA (n=4) 928 PFPeA (n=5) 698 PFHxA (n=6) 1081 PFHpA (n=7) 1186 PFOA (n=8) 4066 PFNA (n=9) 1496 PFDA (n=10) 1407 PFUnA (n=11) 1069 PFDoA (n=12) 1016 PFTrA (n=13) 426 PFTeA (n=14) 587 PFBS (n=4) 654 PFHxS (n=6) 1081 PFOS (n=8) 3507 PFDS (n=10) 340 PFRPA (n=4) 3 PFHpPA (n=6) 33 PFOPA (n=8) 31 PFDPA (n=10) 35 C4/C6 PFPA (n,m=4) 4 C6/C8 PFPA (n,m=6) 12 C8/C8 PFPA (n,m=8) 12 C6/C8 PFPA (n=6 m=8) 8
	PFSAs $(C_nF_{2n+1}-SO_3H)$	
	PFPAAs $(C_nF_{2n+1}-PO_3H_2)$	
	PFPIAs $(C_nF_{2n+1}-PO_2H-C_mF_{2m+1}-R)$	
PFASs	PFECAs & PFESAs $(C_nF_{2n+1}-O-C_mF_{2m+1}-R)$	ADONA $(CF_3-O-CF_2-O-CH_2CH_2-COOH)$ 4 GenX $(C_2F_5-L-CF_2-COOH)$ 26 EEA $(C_2F_5-O-CF_2-O-CF_2-COOH)$ 6 F-53B $(Cl-CF_2-O-CF_2-SO_3H)$ 14 MeFBSA (n=4, R=N(CH ₃) ₂) 25 MeFOSA (n=8 R=N(CH ₃) ₂ H) 134 EtFBSA (n=4 R=N(CH ₃) ₂ H) 7 FfFOSA (n=3 R=N(CH ₃) ₂ H) 259 MeFSE (n=4, R=N(CH ₃) ₂ C ₂ H ₄ OH) 24 MeFSE (n=8 R=N(CH ₃) ₂ C ₂ H ₄ OH) 116 EtFSE (n=4, R=N(CH ₃) ₂ C ₂ H ₄ OH) 4 EtFOSE (n=8 R=N(CH ₃) ₂ C ₂ H ₄ OH) 146 SampAP $(C_2F_5SO_2N(CH_3)C_2H_4OCH_2CH_2OH)$ 8 100s of others
	PASf-based substances $(C_nF_{2n+1}-SO_2-R)$	4,2 FTOH (n=4, R=OH) 106 6,2 FTOH (n=6, R=OH) 375 8,2 FTOH (n=8, R=OH) 412 10,2 FTOH (n=10, R=OH) 165 12,2 FTOH (n=12, R=OH) 42 6,2 diPAP $[C_6F_{13}C_2H_4O_2-PO_2H]$ 23 8,2 diPAP $[C_8F_{17}C_2H_4O_2-PO_2H]$ 25 100s of others
	fluorotelomer-based substances $(C_nF_{2n+1}-C_2H_4-R)$	polytetrafluoroethylene (PTFE) polyvinylidene fluoride (PVDF) fluorinated ethylene propylene (FEP) perfluoroalkoxy polymer (PFA)
	PFAA precursors	
others	fluoropolymers	
	others	

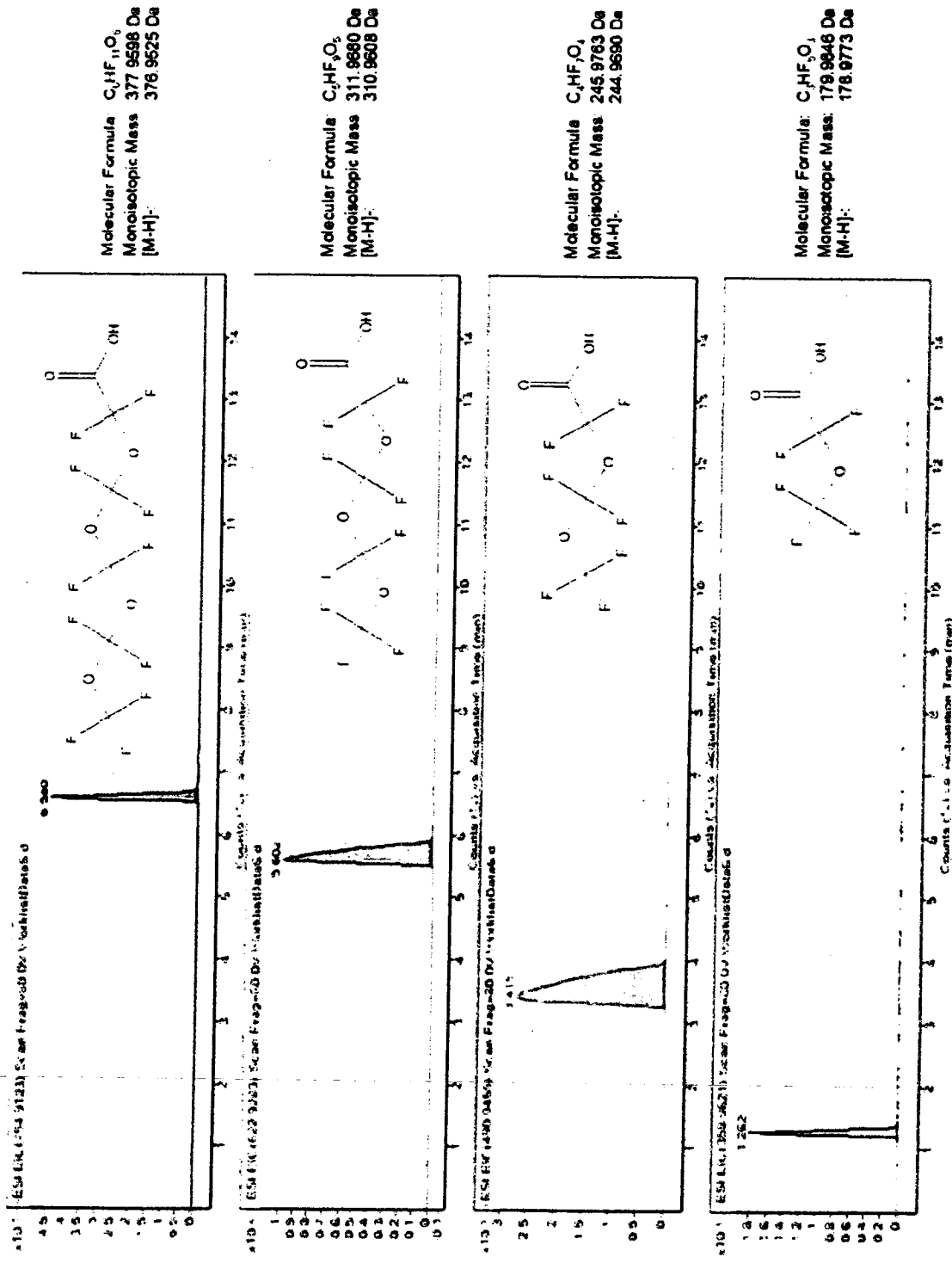
Wang et al. ES&T (2017)

Two series of PFECAs were recently discovered in the Cape Fear River



Strynar et al. ES&T (2015)

Two series of PFECAs were recently discovered in the Cape Fear River

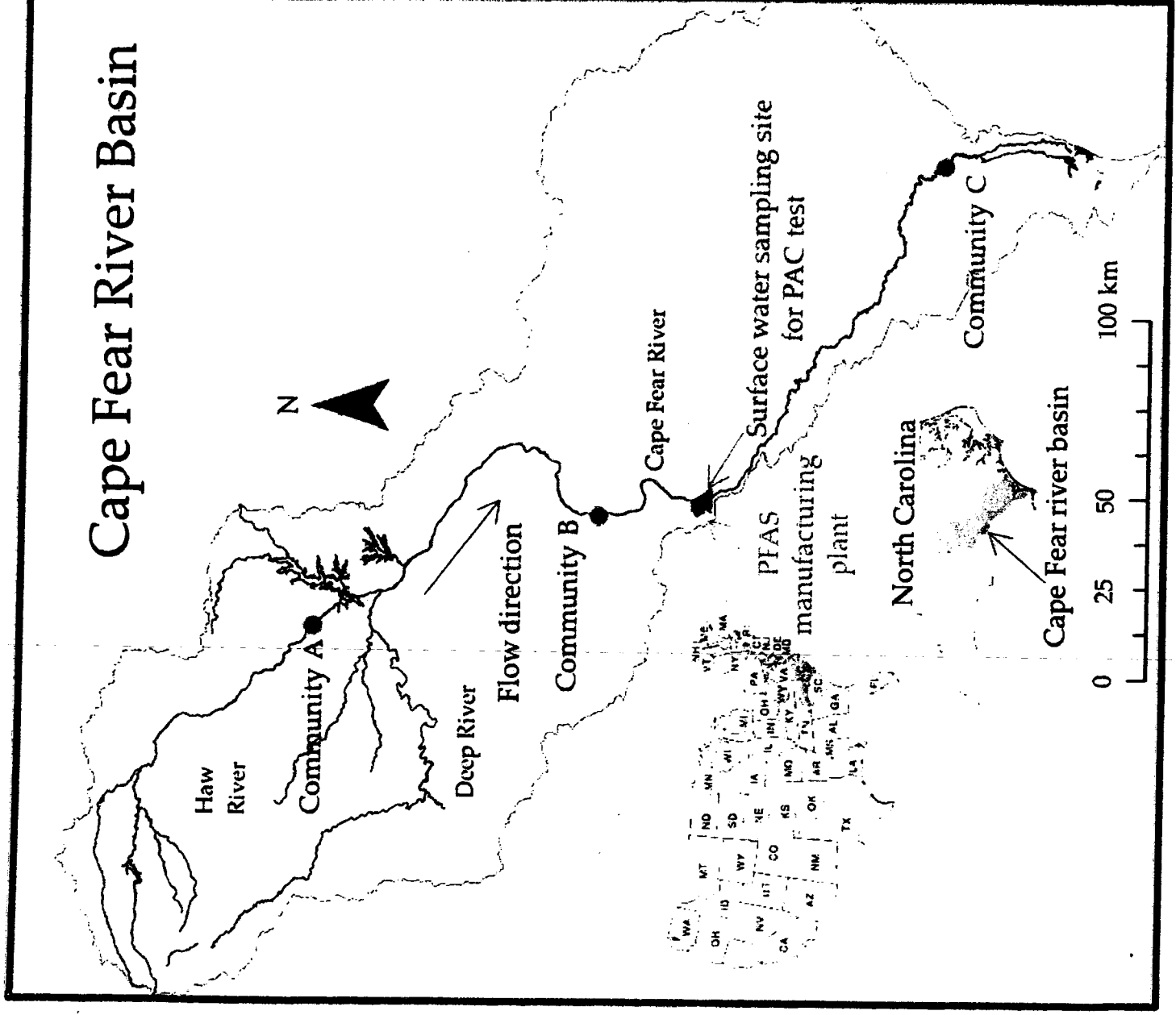


Strynar et al. ES&T (2015)

Study Design

Cape Fear River Basin

- Largest watershed in NC
- Supplies ~1.5M people with drinking water



Sampling Protocol

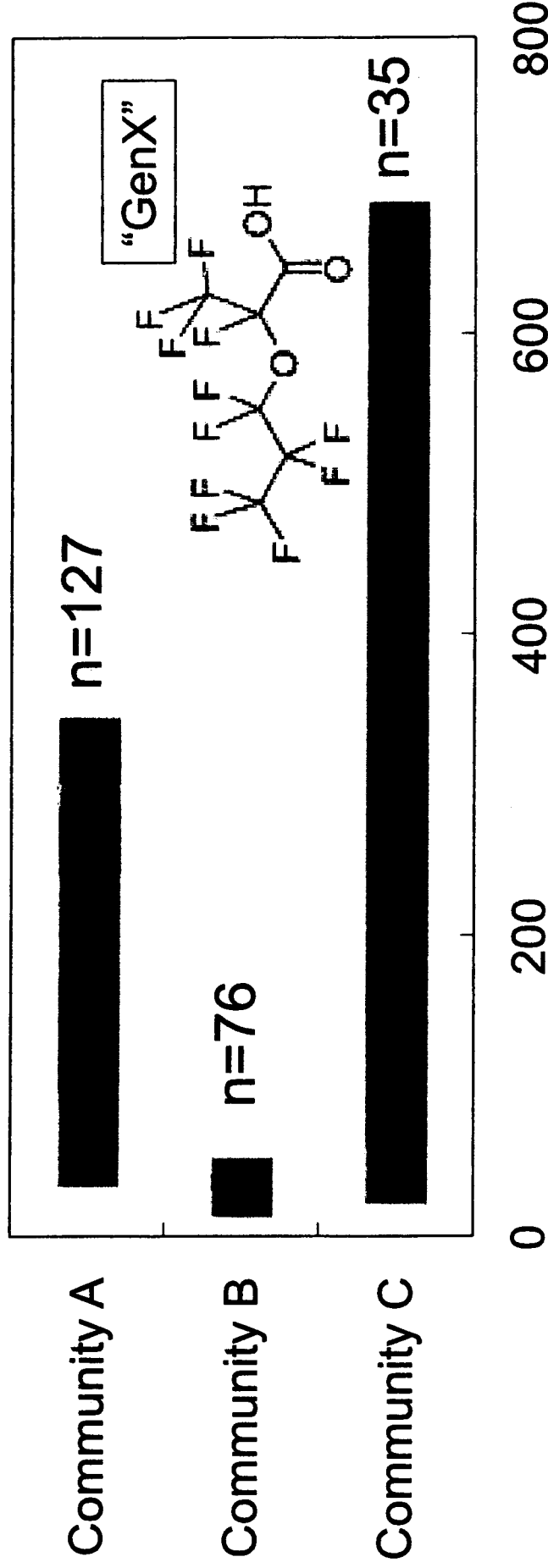
- Samples collected in 1-L HDPE bottles
- Two sampling approaches
 - Daily composite samples of source water at three drinking water treatment plants
 - Grab samples to track PFAS fate in drinking water treatment plant
- No preservative
- Storage at room temperature
- Analysis within 7 days of sample collection

PFAS Analytical Method

- PFAS concentrations measured by LC-MS/MS
- Large-volume direct injection (900 μL)
- Sample and standard preparation:
 - filtration with a 0.45- μm glass fiber filter
 - addition of mass-labeled internal standards
 - addition of formic acid
- Calibration curves ranged from 10 - 750 ng/L
- Limit of quantitation was 10 ng/L for all PFASs except C10 and PFOS (25 ng/L)

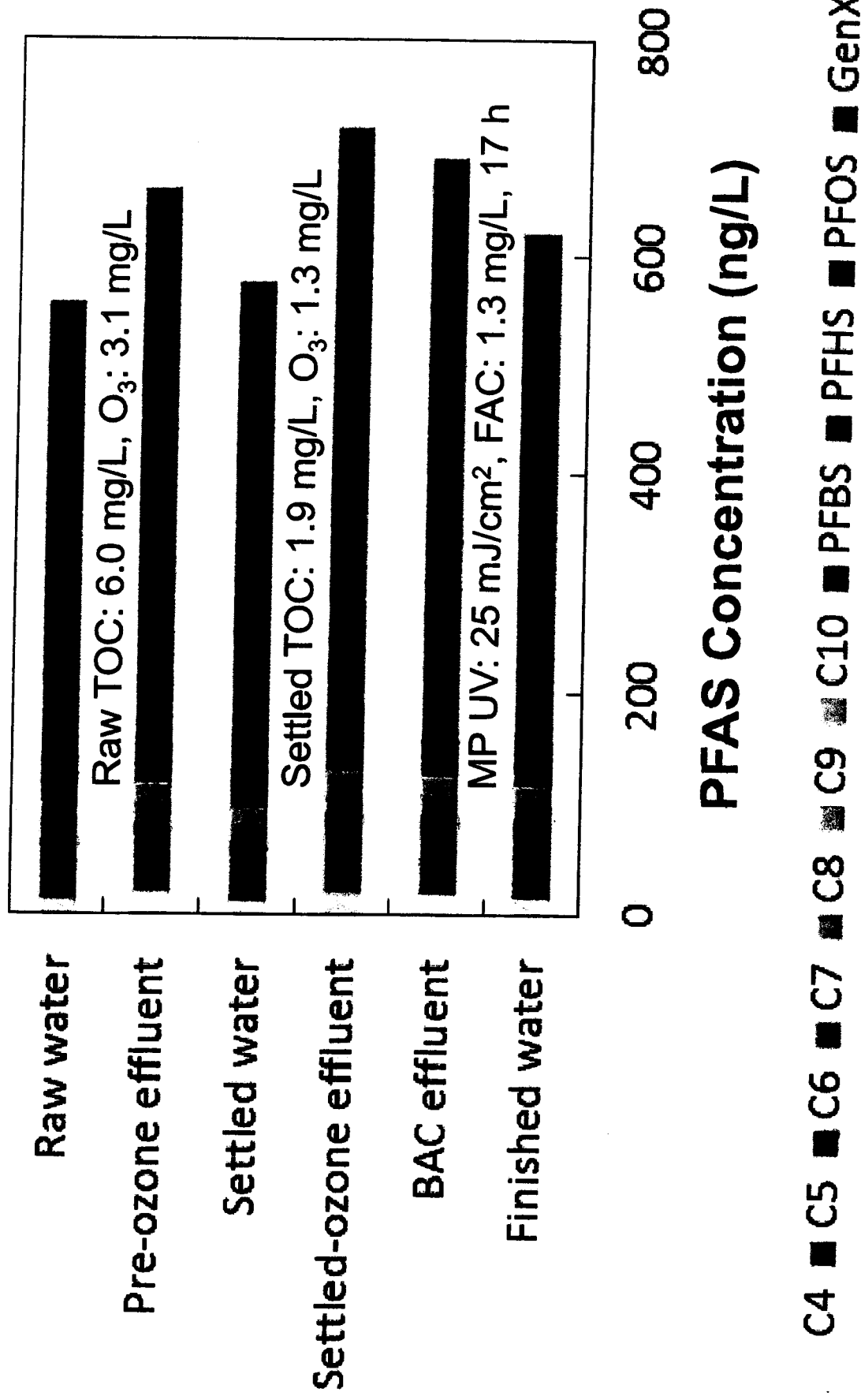
PFAS Occurrence in the CFR Watershed

- PFBA ■ PFPeA ■ PFHxA ■ PFHpA
- PFOA PFNA ■ PFDA ■ PFBS
- PFHxS ■ PFOS ■ PFPrOPrA = "GenX"

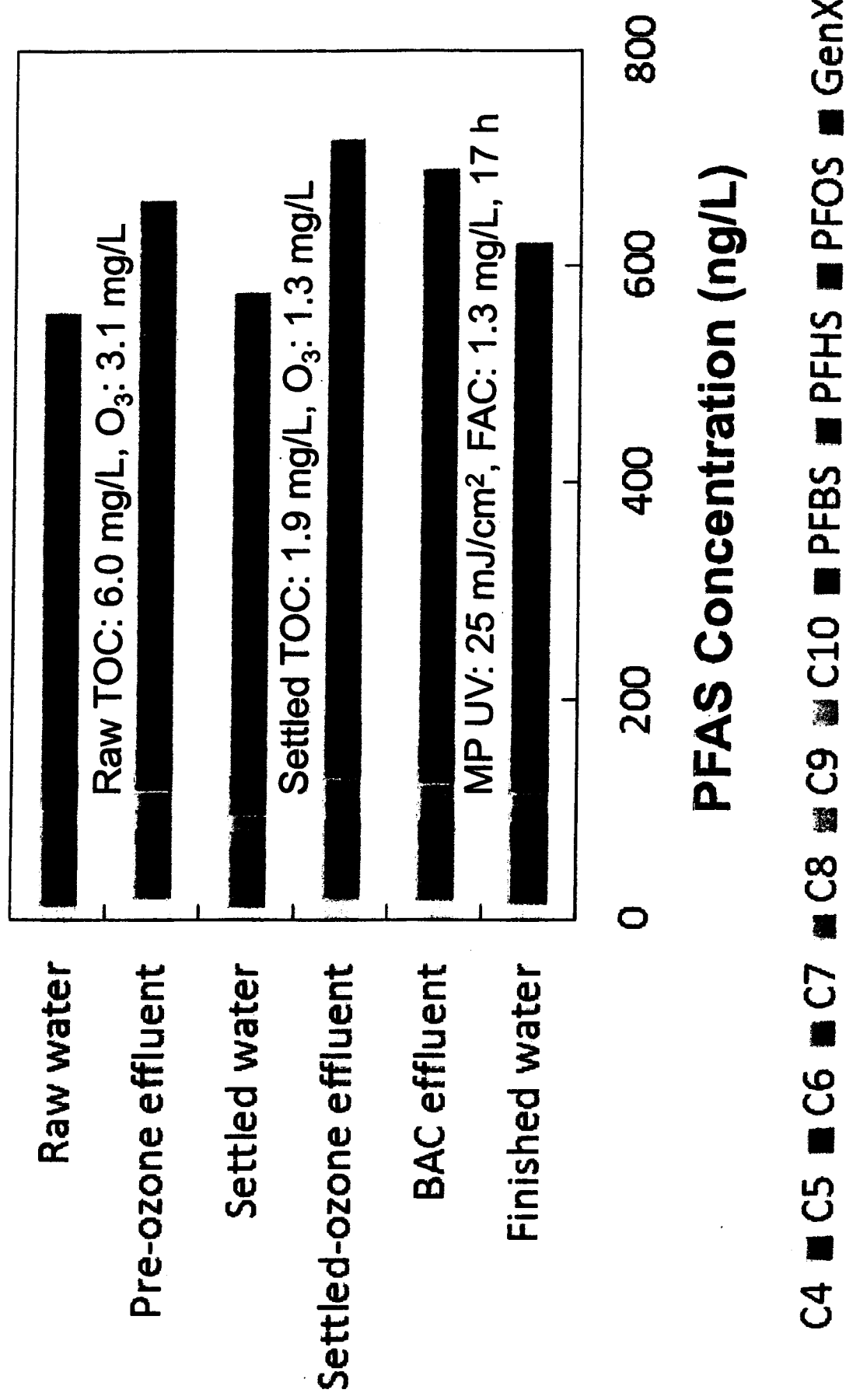


Average concentration in drinking water source (ng/L)

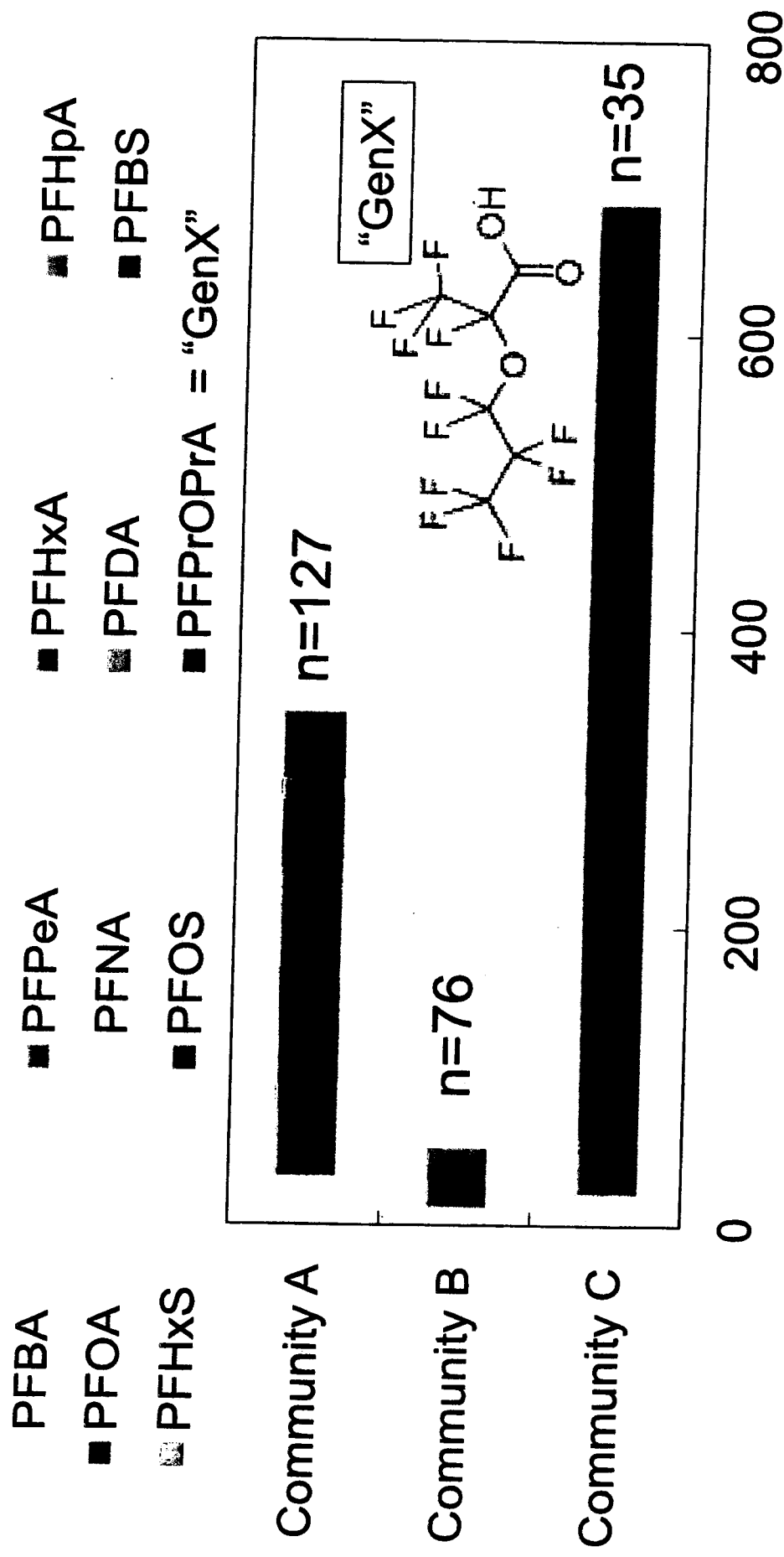
No measurable PFAS removal by conventional and advanced treatment



No measurable PFAS removal by conventional and advanced treatment

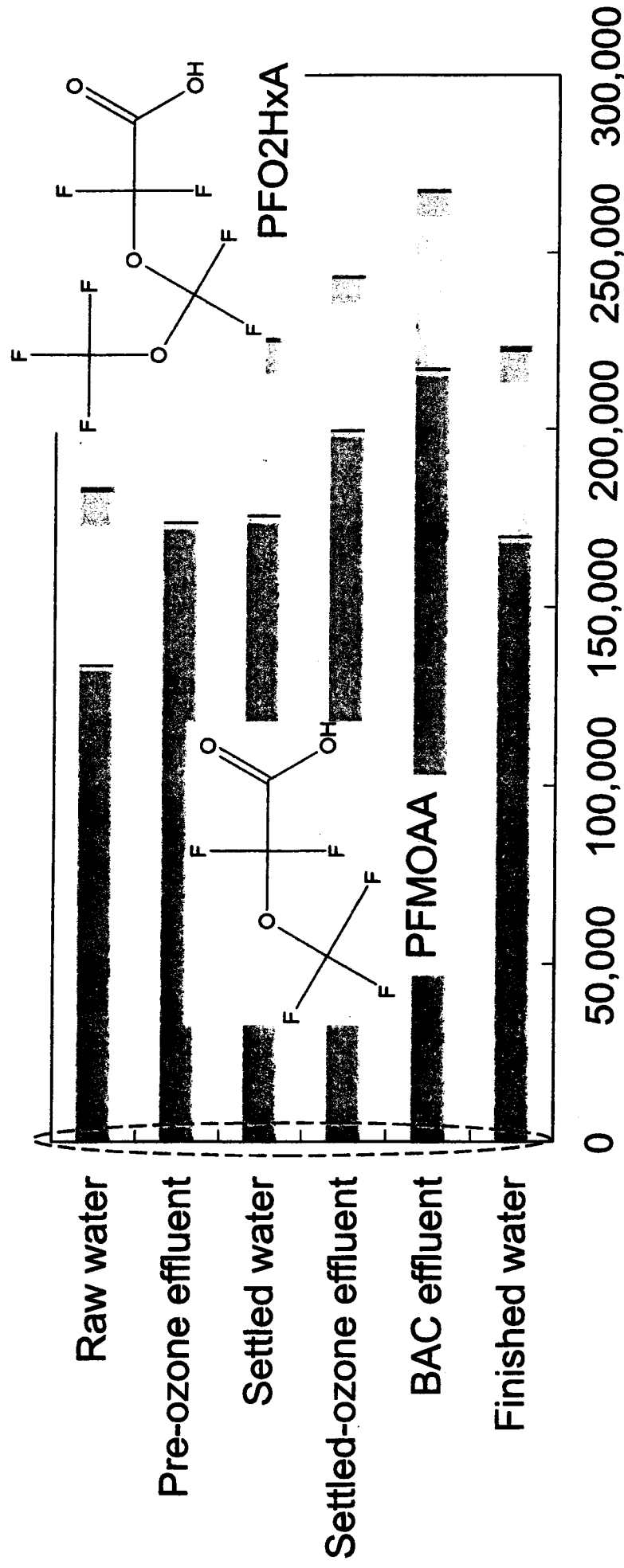


PFAS Occurrence in the CFR Watershed



Average concentration in drinking water source (ng/L)

Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX



Peak area counts of emerging PFASs at a WTP in Community C

■ PFPrOPrA ■ PFMOAA ■ PFMObA ■ PFO2HxA ■ PFO3OA ■ PFO4DA

What about activated carbon?

PAC: thermally activated, wood-based

PAC Doses: 30, 60, 100 mg/L

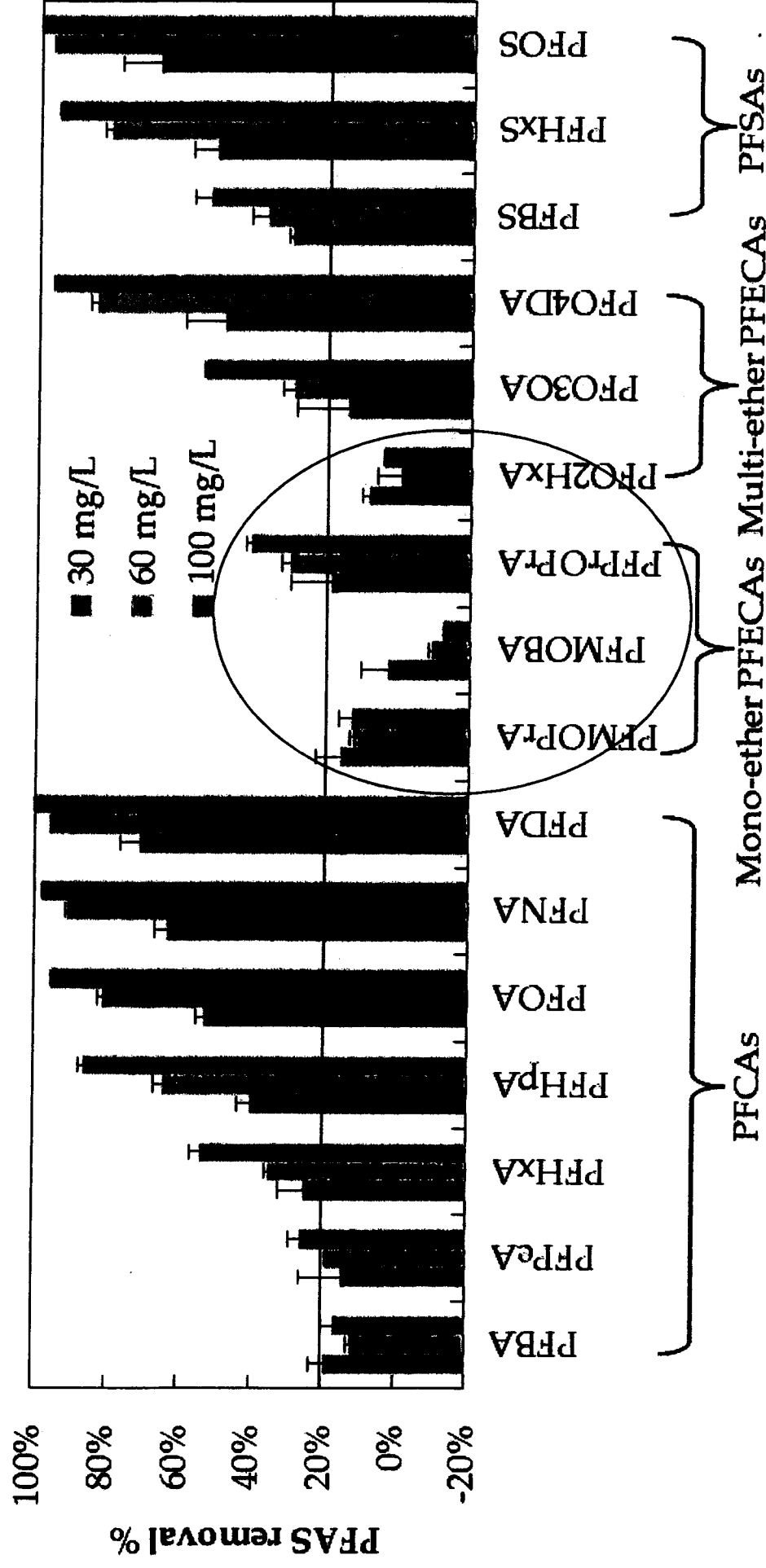
Contact time: 60 minutes

Water: Cape Fear River (TOC: 9.0 mg/L)

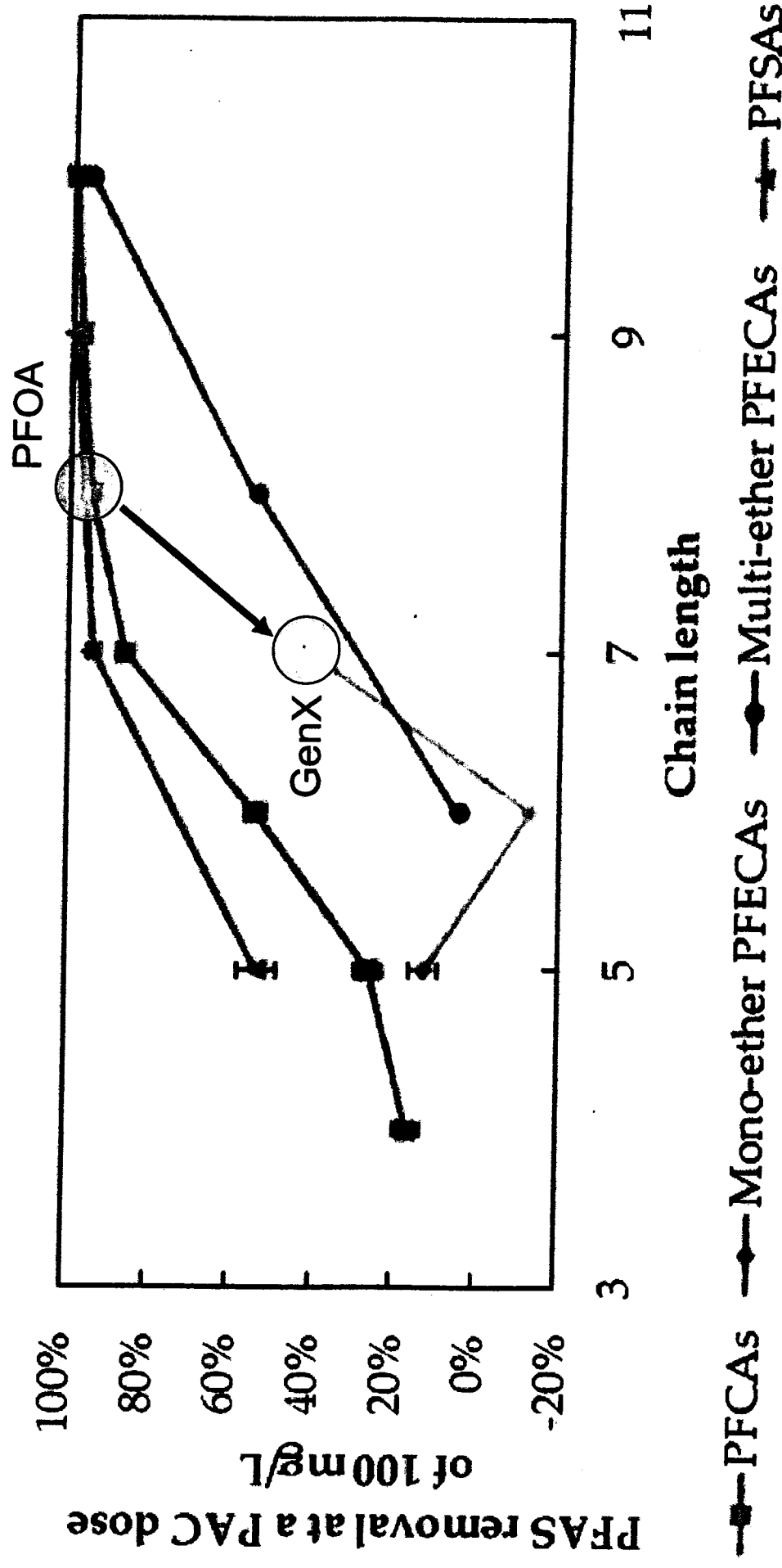
PFECAs: Native levels

PFCAAs and PFSAAs: Spiked at 1000 ng/L

Adsorbability of PFASs varies greatly. The PFECAs that were present at the highest concentrations were essentially non-adsorbable



PFAS adsorbability: PFSA>PFCA>PFECA

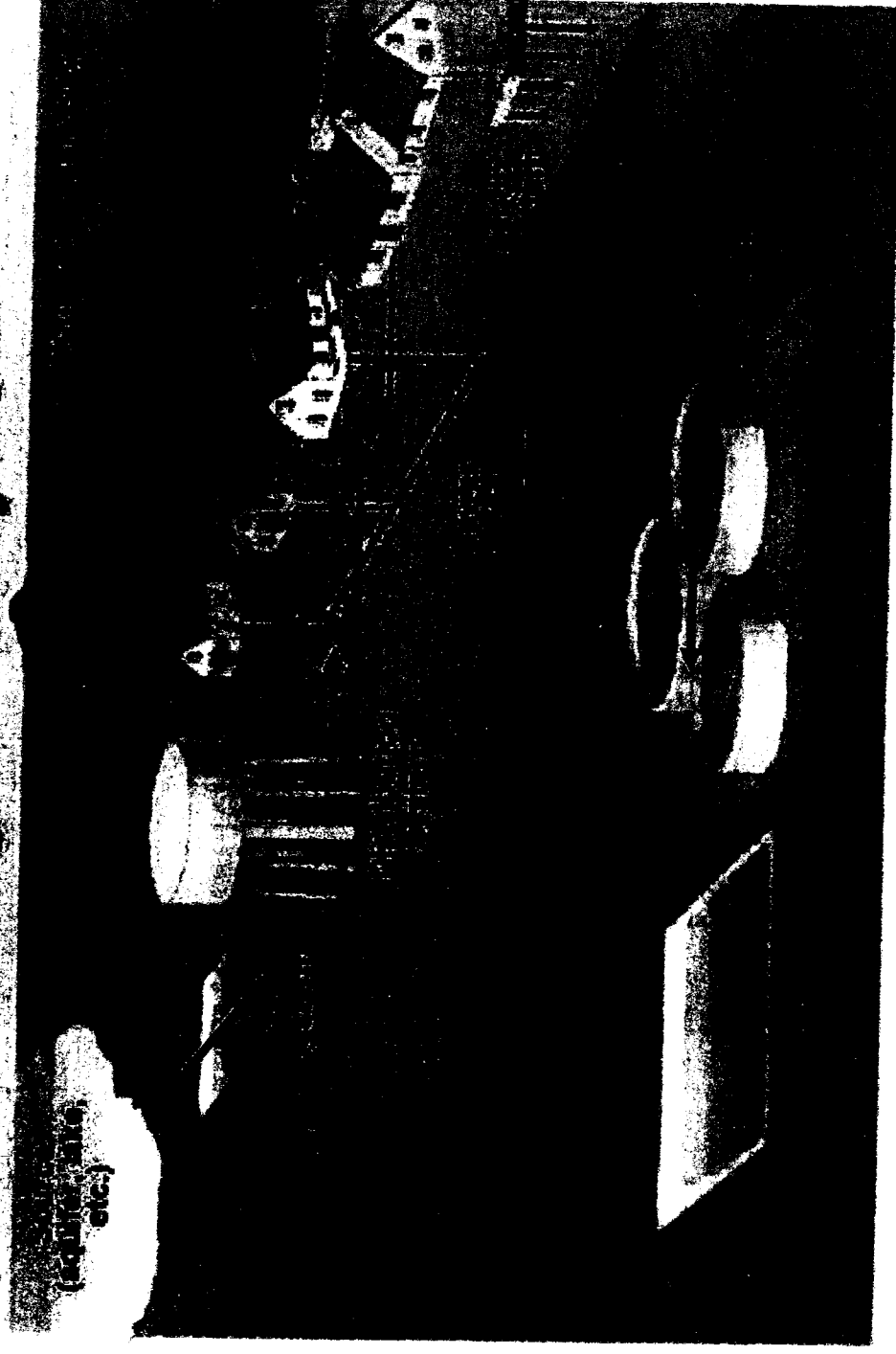


Proposed sampling plan

**1,4-Dioxane and PFAS Fate in
Urban Water Cycle**

Objective 1: Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle

The Drinking Water Cycle



Identify residence times/water ages at suitable sampling points to trace a parcel of water through the water/wastewater system

Objective 2: Determine fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR)

Sample monthly for one ASR cycle (ASR and monitoring wells)

- Recharge
- Storage
- Recovery

Laboratory	Biweekly	Monthly
Cape Fear Public Utilities Authority	Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge)	Total organic carbon, trihalomethanes
NCSU	Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride	1,4-dioxane, PFASs, dissolved organic carbon, UV ₂₅₄ absorbance

Objective 3: Determine possible association of 1,4-dioxane and PFASs with biosolids

Measure 1,4-dioxane and PFAS concentrations in aqueous and solid phases of biosolids. Determine partition coefficients.

Target Audiences for Results

- CFPUA staff
 - Data expected to illustrate treatment/ operational challenges associated with PFASs and 1,4-dioxane
 - Demonstrate need for source control – eliminate PFASs and 1,4-dioxane at upstream NPDES discharge locations
- North Carolina DEQ
 - Raise awareness about treatment challenges with emerging contaminants
 - Expand scope of current 1,4-dioxane working group to start looking at possibilities for controlling PFAS sources

Acknowledgments

- National Science Foundation (Award #1550222)
- North Carolina Urban Water Consortium
- Adam Pickett, Chris Smith, Michael Richardson,
Ben Kearns at participating utilities

CFPUA GenX Research Timeline
6/15/17

May 30, 2014: Mike Richardson received a request from Dr. Knappe for Sweeney, Brunswick, and Pender to do a assessment for the removal of 1,4 dioxane and perfluorinated compounds and a request for the other utility's contact info.

June – August, 2014: Emails between Tiffany Hawley, Mike Richardson, and Dr. Knappe and coordinating meetings and a sampling event for Mid-August.

August 18, 2014: Samples taken at Sweeney Water Treatment Plant for 1,4-dioxane and polyfluorinated ether.

split w/ bromides

October 13, 2014: Email to Mike Richardson proposing intent to write a proposal to NSF 'GOALIE' program to study the occurrence of fluorochemicals in the Cape Fear River and to assess/develop treatment options.

August 26, 2015: Jim Flechtner receives email from Mike Richardson with an NSF proposal to sign.

August 26, 2015: Jim Flechtner signs an intellectual property agreement with NSF and NC State University related to a GOALIE project to be carried out by CFPUA and NC State University under a GOALIE Funding agreement.

May 3, 2016: Mike Richardson receives an email from Dr. Knappe sharing the beginnings of the paper which was shared with Ben Kearns by Mike Richardson.

September 18, 2016: "Manuscript for Review" sent to Mike Richardson and Ben Kearns. The manuscript was written by Dr. Knappe's research group and EPA colleagues for submission to *Environmental Science and Technology Letters*.

September 25, 2016: Ben Kearns replies to Dr. Knappe with no comments on the manuscript. Ben Kearns and Mike Richardson are added as co-authors on the submission.

November 8, 2016: Due to hits on some of the UCMR 3 sampling for PFOAs it was decided to run annual analysis for PFOAs. The first was run on 11/8.

November 10, 2016: The article is published in *Environmental Science and Technology Letters*.

November 18, 2016: Email by Dr. Mallin to various CFRP people Polera, Madison Elise <poleram@uncw.edu>; Beth Eckert <Beth.Eckert@cfpu.org>; Cahoon, Larry <cahoon@uncw.edu>; chad.ham@faypwc.com; Deaton, Anne <anne.deaton@ncdenr.gov>; diana_rashash@ncsu.edu; Fitz Rhode <fritz.rohde@noaa.gov>; kemp@cfw.us; kristina.fischer@ncagr.gov; Mike Giles <mikeg@nccoast.org>; Mike Wicker@fws.gov; nora.deamer@ncdenr.gov; pam.ellis@cfpu.org; janine.harris@noaa.gov; Jennifer Alford <jennifer.b.alford@gmail.com>; slharden@usgs.gov; Saul, Bradley <saubl@live.unc.edu>; Vander Borgh, Mark <mark.vanderborgh@ncdenr.gov>; Prescott, James Carlyle <jcp3677@uncw.edu>. Email only said "Folks – recent CFR paper from NCSU" and attached paper.

Cape Fear River



End of 2016 – Beginning of 2017: Ben Kearns had various conversations with Detleff Knappe regarding GenX, the article, and what are next steps.

March 6, 2017: Dr. Knappe and Ben Kearns discussed the Perfluorinated chemicals in the river and its fate through Sweeney and some potential additional research on the PFOAs and GENx with additional samples.

March 7, 2017: Ben Kearns sent a copy of the article to Beth Eckert and other CFPWA staff for review and discussion as background for evaluating participation in the next phase.

March 8, 2018: Beth Eckert gave a copy of the article to Frank Styers for review. Beth went to give Mike McGill a copy and he stated he had already gotten a copy from Ben. Beth and Frank discussed the paper and determined we needed to meet with Jim Flechtner. Frank gave Jim a copy of the paper.

March 20, 2017: Beth, Frank, Carel, and Jim met and talked about the article and the request for additional research. Determined that we needed more information and that Dr. Knappe needed to provide a scope and request for us to review next steps. Need to address each research opportunity and its findings on a case by case basis. Frank made the request of Ben to coordinate this request.

April 13
Early April: Meeting with Frank Styers, Beth Eckert, Ben Kearns, and John Malone to discuss Dr. Knappe's desire for more research, pros, cons and what we need for him to provide to improve our understanding of the previous paper and next steps.

April 13, 2017: Ben Kearns sent information informing everyone that attends the Water Team Meeting (Jim Flechtner <jim.flechtner@cfpua.org>; Frank Styers <Frank.Styers@cfpua.org>; Carel Vandermeiden <Carel.Vandermeiden@cfpua.org>; Jim Tayson <Jim.Tayson@cfpua.org>; Elizabeth Severt <Elizabeth.Severt@cfpua.org>; William Roy <William.Roy@cfpua.org>; Craig Wilson <Craig.Wilson@cfpua.org>; Allyson Ridout <Allyson.Ridout@cfpua.org>; Overby, Tommy D <tommy.overby@ncdenr.gov>; 'heidi.cox@ncdenr.gov'; Steve Mongeau <steve.mongeau@cfpua.org>; Gary McSmith <Gary.Mcsmith@cfpua.org>; Mike McGill <Mike.McGill@cfpua.org>; Justin Maurice <Justin.Maurice@cfpua.org>; Eric Hatcher <eric.hatcher@cfpua.org>; Beth Eckert <Beth.Eckert@cfpua.org>; Rebecca Cramer <Rebecca.Cramer@cfpua.org>; Maggie Butler <Maggie.Butler@cfpua.org>; Phil Brower <Phil.Brower@cfpua.org>) that he had coordinated with Dr. Knappe to come to our Water Team meeting on April 19, 2017 to do a presentation on PFOAs and GenX and the methodology of how the data was analyzed and what the next steps are for research and potential regulation.

April 19, 2017: Dr. Knappe came to Sweeney to attend our water team meeting and did a presentation on PFOAs, PFOS, and GenX and the previous research. He discussed his methodologies and the collaboration with peers and EPA. He also outlined what he would like to do for his next project to further investigate GENX and its fate and look for potential treatment technologies and to use the research to talk to the State of NC to get it regulated and out of the river. Attendees at this meeting included various areas of CFPWA, Dr. Knappe and Heidi Cox of NCDEQ – PWS. Heidi noted that she would pass along the info to her counterparts at the state.

April 20, 2017: Dr. Knappe provided a copy of the presentation from the meeting to CFPWA staff for review.

Mid April: Staff looked up research on GenX and PFOAs and its human health effects. Everything that was identified, stopped short of true answers, most said its less harmful than the predecessor PFOAs, while another stated the opposite, and most all said more information and study is needed to determine what if any health effects are associated with the product.

April 24, 2017: Jill Deaney forwarded an Abstract to Beth Eckert comparing the potency of vivo PFAS alternatives and their predecessors.

April 27, 2017: Beth Eckert contacted Jim Gregson at NCDEQ to find out if Chemours was regulated from their office and what he knew about the company and their discharge. He sent us a copy of their NPDES permit, cover letter, change of ownership, and fact sheet.

May 2, 2017: Discussed with Linda Culpepper while at the ESI partnership meeting the process we would go through to get the state's assistance to further investigate and regulate, if necessary, the discharge of a new chemical GenX that is discharged by Chemours upstream of our discharge. Discussed the Dr. Knappe research and the fate at the end of treatment and our concerns. She gave a brief overview of the process and gave me the name of someone in Fayetteville regional office named Trevor and to let her know if she can help.

add to notes
Mid May 2017: Had more discussions with Jim Gregson and he asked if there was anything he could do to assist. I told him we were trying to figure out what we had, what impacts were there or not, and what our next steps were. That we would likely be sending a formal request for assistance. He said if he can help to let him know. At the request of Jim Flechtner, Frank Styers and Beth Eckert drafted a letter for his signature, and the Board's approval, requesting assistance in evaluating and regulating, if necessary, the discharge to the river. Ben Kearns forwarded additional research information on GenX and its toxicity information. Dr. Knappe notified Ben Kearns that he had been contacted by Star News about the research. Mr. Styers contacted Dr. Knappe on multiple occasions to further discuss and understand the report and GenX's its potential impacts.

June 1, 2017: Star News Contacted CFPWA regarding the Dr. Knappe report and Frank Styers discussed the report with Mr. Haggerty and provided him answers to his questions on the next day.

June 2, 2017: Beth Eckert spoke to Dr. Knappe about the research, next steps, who he had spoken with at the State, what he knew about Chemours and the process. He stated that he had contacted Chemours and he had contacted NCDEQ. He stated that based on his research in to their permit renewal application that the waste from the GenX process is listed as being hauled away and was wondering why it was still in the water if that is the case. He stated that we just needed to meet with Chemours and make them stop discharging the GenX like what had happened with the 1,4-Dioxane issue a few years back. I relayed to him that we do not regulate Chemours and we had to go through the state and that we had drafted a letter requesting the state's assistance. He said if he can help to let him know and that he was going to be meeting with Chemours permit writer as well.

June 5, 2017: Staff met to discuss questions, letters, response, and board notification.

June 7, 2017: Jim Flechtner briefed the Executive Committee and received approval to send previously drafted letter to NCDEQ. Staff sent the NCDEQ letter via e-mail and postal service to NCDEQ. StarNews Article was published online.

June 8, 2017: Star News article published in newspaper. Staff and in house Legal Counsel had multiple meetings regarding CFPUA response, press release, and FAQs for staff responses when fielding calls. Mr. Flechtner spoke to Sheila Holman, Assistant Secretary of NCDEQ, to follow up on the letter and discuss their response and a time frame. Ms. Eckert contacted Mr. Gregson and asked if he had access to the Chemours renewal packet and what information NCDEQ had when they were evaluating the permit. Mr. Gregson sent back a link to the Chemours application that is on the states site and a study by Dr. Beekman that indicated the GenX is less harmful than its predecessor and stated Sergei was the permit writer from 2011 and that he may know more. Ms. Eckert spoke to Julie Gryzb, NCDEQ Complex Permitting Supervisor, regarding the permit renewal status of Chemours. She stated they were aware of the GenX issue we were facing and a permit writer had been assigned, but it would take probably a month or two for the person to start the permit. She stated it would probably take that time to more fully understand the issues and their potential impacts. Ms. Eckert asked what we needed to do to speed up the process and she stated that they needed the time to more fully understand it. Mr. Flechtner hired a communications person to draft an OP Ed and to get it placed in Star news on CFPUAs position.

June 9, 2017: Staff had multiple meetings to further discuss communications, both internal and external and messaging. Mr. Flechtner and the Chairman began collaborating with the City and County on a joint response entailing NCDEQ, EPA, Department of Health, Political Representatives and Chemours. They also attended a conference call with Chemours and the County representatives. Reviewed and commented on the op ed and drafted a press release on CFPUAs position and actions about the study and GenX. Mr. Flechtner hired Brooks Pierce as an environmental legal consultant to research our options and to write a resolution for the board. Staff discussed options with the counsel.

Weekend: Continued to field calls for the public and the op ed was published in Sundays Star News.

June 10, 2017: Made multiple attempts to contact Detleff Knappe with clarification questions on the report. CFPUA Staff, Board members, County Staff (County Manager, Department of Public Health, and PIO), and County Commissioners met to further discuss the Genx, what we know, what we don't and next steps. Established timeline and logistics of meeting to occur on Thursday here in Wilmington with Chemours, NCDEQ, County, CFPUA and City representatives. Spoke to counsel who asked for clarification on some of the questions about the published report. At time of finalizing this timeline, staff had received no response from Dr. Knappe to clarify this information. Mr. Flechtner, in house counsel, and Board Chairman interviewed Crisis Communication entities. Notified by NCDEQ of the results of their conference call with Chemours at the end of the day. NCDEQ will be collecting samples over the next 3 weeks at the river and affected entities finished water locations. These samples will be sent to a lab in Colorado. They will be coordinated and collected by NCDEQ but paid for by Chemours.

Completed timeline as of EOD 6/10/17. Updated 6/15/17.

Jill Deaney

From: Jill Deaney
Sent: Monday, June 12, 2017 5:28 PM
To: Beth Eckert
Subject: FW: Perfluorinated chemicals in the Cape Fear River

From: Jill Deaney
Sent: Monday, March 06, 2017 10:05 AM
To: Ben Kearns <ben.kearns@cfpua.org>
Cc: Jill Deaney <jill.deaney@cfpua.org>; Allyson Ridout <allyson.ridout@cfpua.org>; Adam.Poore@cfpua.org
Subject: RE: Perfluorinated chemicals in the Cape Fear River

Ben,

Below is a summary of our detects for the Perfluorinated compounds which were analyzed using EPA method 537.

The first four samples were included in our UCMR3 monitoring.

Based on our results, in October 2016 we decided to begin special sampling on the Post CW with the first sample scheduled for November 2016 and then annually in September which was the month the results were the highest.

We have not tested our raw water to see if we have any removal so we could add the raw site to our annual sample.

Sample date	Sample location	Perfluoroheptanoic Acid (PFHpA) (µg/L)	Perfluorooctanoic acid (PFOA) (µg/L)
12/5/2013	Post CW	0.014	ND
3/11/2014	Post CW	ND	ND
6/9/2014	Post CW	0.012	ND
9/8/2014	Post CW	0.027	ND
11/8/2016	Post CW	0.013	0.013

Next test scheduled for Post CW for September 2017.

Jill

-----Original Message-----

From: Ben Kearns
Sent: Monday, March 06, 2017 9:20 AM
To: Jill Deaney <Jill.Deaney@cfpua.org>
Subject: RE: Perfluorinated chemicals in the Cape Fear River

No worries.

I wanted to simply make the opportunity available to you if you had questions you would like to ask Dr. Knappe. If you have any questions feel free to forward them to me and I will be sure and ask him. I thought that between the two of us we could make it a very productive and insightful conversation regarding these contaminants of emerging concern.

I received your voice mail.

The only sample we have of CFPUA finished water is from August 18, 2014. GenX was 474 ng/L.

We have raw water samples for the following dates. These were composited daily samples.

Date	GenX (ng/L)
6/14/13	55.1
6/15/13	69.45
6/16/13	98.6
6/17/13	127.5
6/18/13	178
7/3/13	334
7/4/13	210.5
7/5/13	127
7/6/13	127
7/7/13	132.5
7/8/13	147
7/10/13	193.5
7/11/13	272
7/12/13	326
7/13/13	303
7/14/13	241.5
7/15/13	187.5
9/25/13	4560
9/26/13	3080
9/27/13	2200
9/28/13	1990
9/29/13	1575
9/30/13	863
10/1/13	567
10/2/13	577.5
10/4/13	368
10/5/13	369
10/6/13	334
10/7/13	354
10/8/13	307
10/9/13	327
10/10/13	275
10/11/13	266
10/13/13	305

In addition, we have a grab sample from the river from December 16, 2016 that was collected at Tar Heel. GenX was 172 ng/L.

Nov 2013 installed
Abatement

were they producing
the week of 12/14

Summary of “Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina” by Dr. Knappe published on November 10, 2016.

The purpose of the study:

- To determine the presence of legacy long-chain and recently discovered short-chain Perfluorinated compounds in the Cape Fear River,
- To study if these compounds can be removed by water treatment processes
- How much of the compounds can be adsorbed/removed using powdered activated carbon (PAC).

Background information about legacy long-chain fluorinated substances:

- Long-chain fluorinated substances (PFASs) are used in manufacturing of plastics, water/stain repellents, firefighting foams and food-contact paper coatings.
- Legacy (long chain) PFOA and PFOS have been evaluated by EPA and established a lifetime health advisory level (HAL)* of 70 ng/L for the sum of PFOA and PFOS concentrations in drinking water.
- Due to the growing concern over the legacy PFOA/PFOS over the past decade, manufacturers have replaced these compounds with short-chain fluorinated compounds.

Summary of the Sampling:

- Data was collected at three water treatment facilities on the Cape Fear River referred to as Communities A, B, and C.
- The data for Communities A and B indicated only the presence of the legacy long chain PFASs.
- Community A: Of the 127 samples collected of raw water, 57 exceeded the EPA HAL of 70 ng/L with the average of all samples being 90 ng/L. (PFOS+PFOA)
- Community B: Of the 73 samples collected of raw water, the average of all samples was 59 ng/L. (PFOS+PFOA). This suggests there are no facilities between communities’ A and B that discharge PFASs.
- Community C, CFPWA Sweeney Water Treatment Plant (SWTP):
 - Of the 34 samples collected of raw water, the levels of the PFASs were much higher and showed a presence of both the legacy long chain PFOS+PFOA and the new emerging short chain PFASs.
 - The legacy compounds were in small concentrations and well below the EPA HAL.
 - The largest concentration of the PFASs identified in the raw water was a compound known by the trade name GenX. GenX is produced by a chemical manufacturer, Chemours. The facility is located upstream of Community C and downstream of Community B.
 - The average concentrations of the GenX compound found in the raw water intake was 631 ng/L.
 - Although no HAL exist for GenX the observed raw water concentration was measured at ~8x the HAL for PFOS+PFOA
 - The highest concentrations were observed at low flow periods into the treatment facility.
 - A single sampling event occurred on August 18, 2014 where grab samples were taken at various treatment processes throughout the plant from the raw water intake to the finished water.

Summary of Treatment Effectiveness:

- This single sampling event through the SWTP did not show any removal of the fluorinated compounds through the plant processes.
 - The Researcher notes the changes between treatment processes may be related to changes in the source water that occur in the time frame corresponding to the hydraulic residence time at the DWTP.
- The study found the use of powdered activated carbon (PAC) is effective in removing longer chain Perfluorinated compounds but much less effective in shorter chain compounds.

Summary of Information on GenX:

- GenX was the replacement for the legacy long chain PFASs used in the manufacturing process at Chemours.
- The report states there is no published data about removal of GenX through drinking water treatment
- It also notes there is little known about the toxicity or environmental effects of GenX.
- Researcher noted, of the few studies, most were done by the manufacturer.
- GenX has been used at the Chemours facility since 2010.

Researcher What's Next:

- The study concludes due to high levels of emerging PFAS there is a need to begin routine monitoring.
- More study is needed to determine health effects and to further identify if any treatment processes are effective.
- Broader discharge control and contaminant monitoring is needed.

CFPUA Questions from the study:

- What, if any, health effects are associated with GenX?
- If health effects exist, what level is a concern?
- Information staff researched indicated short chained GenX is less harmful than the legacy compounds, but that more research is needed to fully understand effects. It was listed as a category 2 possible human carcinogen.
- Limited data points, only 1 event on SWTP processes and finished water.
- The GenX chemical is not included in the any EPA certified method so how accurate was the testing?
- Are there any commercial labs that can test for it?
- How is this regulated and is Chemours aware it is being detected downstream and in the drinking water?
- What did the state know and how could they help us get the answers we needed to protect public health?
- States perspective on how would we go about getting this discharge evaluated based on this information and removed or reduced to eliminate any health concerns downstream?
- Data was collected in 2013, other than the one 2014 sampling event, and Chemours installed new abatement technology in November 2013, is it still a problem?

** Health Advisory definition:*

- *EPA's health advisories are non-enforceable and non-regulatory and provide technical information to states agencies and other public health officials on health effects, analytical methodologies, and treatment technologies associated with drinking water contamination. EPA's health advisory level for PFOA and PFOS offers a margin of protection for all Americans throughout their life from adverse health effects resulting from exposure to PFOA and PFOS in drinking water.*

John Malone

From: Mike McGill
Sent: Wednesday, August 10, 2016 1:20 PM
To: Michael Richardson; Beth Eckert; Jim Flechtner
Subject: We may have to deal with this... Our area is highlighted.

Importance: High

not sent

Look at the map. This is the Harvard release. I've cut and pasted it below...

Mike

<https://www.hsph.harvard.edu/news/press-releases/toxic-chemicals-drinking-water/>

Unsafe levels of toxic chemicals found in drinking water for six million Americans

water-faucet

Drinking water samples near industrial sites, military fire training areas, wastewater treatment plants have highest levels of fluorinated compounds

For immediate release: August 9, 2016

Boston, MA – Levels of a widely used class of industrial chemicals linked with cancer and other health problems—polyfluoroalkyl and perfluoroalkyl substances (PFASs)—exceed federally recommended safety levels in public drinking water supplies for six million people in the U.S., according to a new study led by researchers from Harvard T.H. Chan School of Public Health and the Harvard John A. Paulson School of Engineering and Applied Sciences (SEAS).

The study will be published August 9, 2016 in Environmental Science & Technology Letters.

“For many years, chemicals with unknown toxicities, such as PFASs, were allowed to be used and released to the environment, and we now have to face the severe consequences,” said lead author Xindi Hu, a doctoral student in the Department of Environmental Health at Harvard Chan School and Environmental Science and Engineering at SEAS. “In addition, the actual number of people exposed may be even higher than our study found, because government data for levels of these compounds in drinking water is lacking for almost a third of the U.S. population—about 100 million people.”

PFASs have been used over the past 60 years in industrial and commercial products ranging from food wrappers to clothing to pots and pans. They have been linked with cancer, hormone disruption, high cholesterol, and obesity. Although several major manufacturers have discontinued the use of some PFASs, the chemicals continue to persist in people and wildlife. Drinking water is one of the main routes through which people can be exposed.

The researchers looked at concentrations of six types of PFASs in drinking water supplies, using data from more than 36,000 water samples collected nationwide by the U.S. Environmental Protection Agency (EPA) from 2013–2015. They also looked at industrial sites that manufacture or use PFASs; at military fire training sites and civilian airports where fire-fighting foam containing PFASs is used; and at wastewater treatment plants. Discharges from these plants—which are unable to remove PFASs from wastewater by standard treatment methods—could contaminate groundwater. So could the sludge that the plants generate and which is frequently used as fertilizer.

Credit: Hu et al, Environmental Science & Technology Letters <http://pubs.acs.org/doi/pdf/10.1021/acs.estlett.6b00260>

The study found that PFASs were detectable at the minimum reporting levels required by the EPA in 194 out of 4,864 water supplies in 33 states across the U.S. Drinking water from 13 states accounted for 75% of the detections, including, in order of frequency of detection, California, New Jersey, North Carolina, Alabama, Florida, Pennsylvania, Ohio, New York, Georgia, Minnesota, Arizona, Massachusetts, and Illinois.

Sixty-six of the public water supplies examined, serving six million people, had at least one water sample that measured at or above the EPA safety limit of 70 parts per trillion (ng/L) for two types of PFASs, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). Concentrations ranged as high as 349 ng/L for PFOA (Warminster, PA) and 1,800 ng/L for PFOS (Newark, DE).

The highest levels of PFASs were detected in watersheds near industrial sites, military bases, and wastewater treatment plants—all places where these chemicals may be used or found.

“These compounds are potent immunotoxicants in children and recent work suggests drinking water safety levels should be much lower than the provisional guidelines established by EPA,” said Elsie Sunderland, senior author of the study and associate professor in both the Harvard Chan School and SEAS.

Other Harvard Chan authors of the study included Philippe Grandjean and Courtney Carignan.

Funding for the study came from the Smith Family Foundation and a private donor.

“Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants,” Xindi C. Hu, David Q. Andrews, Andrew B. Lindstrom, Thomas A. Bruton, Laurel A. Schaider, Philippe Grandjean, Rainer Lohmann, Courtney C. Carignan, Arlene Blum, Simona A. Balan, Christopher P. Higgins, and Elsie M. Sunderland, *Environmental Science & Technology Letters*, online August 9, 2016, doi: 10.1021/acs.estlett.6b00260

PFASs and reduced immune response

Another Harvard Chan School study, led by Grandjean, adjunct professor of environmental health, published in *Environmental Health Perspectives*, also suggested negative health impacts of PFAS exposure. That study looked at a group of about 600 adolescents from the Faroe Islands, an island country off the coast of Denmark. Those exposed to PFASs at a young age had lower-than-expected levels of antibodies against diphtheria and tetanus, for which they had been immunized. The findings suggested that PFASs, which are known to interfere with immune function, may be involved in reducing the effectiveness of vaccines in children.

Funding for this study came from the National Institute of Environmental Health Sciences, NIH (ES012199); the U.S. Environmental Protection Agency (R830758); the Danish Council for Strategic Research (09-063094); and the as part of the environmental support program DANCEA (Danish Cooperation for Environment in the Arctic).

“Serum Vaccine Antibody Concentrations in Adolescents Exposed to Perfluorinated Compounds,” Philippe Grandjean, Carsten Heilmann, Pal Weihe, Flemming Nielsen, Ulla B. Mogensen, and Esben Budtz-Jørgensen, *Environmental Health Perspectives*, online August 9, 2016, doi: 10.1289/EHP275

Mike

Mike McGill
Chief Communications Officer
Cape Fear Public Utility Authority (CFPUA)
Stewardship. Sustainability. Service.

Office: (910) 332-6704
After hours: (910) 622-8472
mike.mcguill@cfpua.org
communications@cfpua.org

John Malone

From:

Sent:

To:

Subject:

Detlef Knappe <knappe@ncsu.edu>

Friday, May 30, 2014 8:01 AM

Michael Richardson

Brunswick and Pender

1st mention of a study!

Mike,

I think it would be interesting to do a full-scale assessment of Sweeney, Brunswick, and Pender for 1,4-dioxane and perfluorinated compound removal. The idea of having three plants with very different treatment approaches treating essentially the same source provides a unique opportunity to get a quick assessment of a wide range of treatment technologies. Would you be willing to plant the seed with Brunswick and Pender? Also, can you send me contact info for the folks in charge at Brunswick and Pender? Everyone would have to be comfortable that some of the analyses would be conducted at an EPA research lab...

Thank you,

Detlef

--
Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://www4.ncsu.edu/~knappe>

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Tuesday, July 01, 2014 8:25 AM
To: Tiffanie Hawley; Michael Richardson
Subject: Re: Sampling for polyfluorinated ethers

Thank you, Tiffany. Please let me know what you hear from Glenn Walker.
Ideally, we would accomplish two things with a trip to Sweeney:

- 1. Explain the research
- 2. Take samples

Best,
Detlef

On 6/24/14 10:39 AM, Tiffanie Hawley wrote:

> Detlef, I didn't see where I responded to you last week - my bad.

> I did hear back from Brandon Garner at Pender Co, and he is interested in a meeting here at Sweeney to hear you explain the research, but I haven't heard from Glenn Walker at Brunswick yet...

> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Thursday, June 19, 2014 11:35 AM

> To: Michael Richardson; Tiffanie Hawley

> Subject: Sampling for polyfluorinated ethers

> Mike and Tiffany,

> It was good to see you yesterday... Can you send me contact info for the Brunswick Co. and Pender Co. plants?

> Thank you,

> Detlef

>

> --

> Detlef Knappe

> Professor

> 319-E Mann Hall

> Department of Civil, Construction, and Environmental Engineering North

> Carolina State University Campus Box 7908 Raleigh, NC 27695-7908

> Phone: 919-515-8791

> Fax: 919-515-7908

> E-mail: knappe@ncsu.edu

> Web page: <http://www4.ncsu.edu/~knappe>

>

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Detlef Knappe

Professor

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Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
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Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://www4.ncsu.edu/~knappe>

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Wednesday, August 13, 2014 10:58 AM
To: Tiffanie Hawley; Michael Richardson
Subject: Re: Sampling for polyfluorinated ethers

Hi Tiffany and Mike,

Can my post-doc (Mei Sun) and two EPA researchers (Andrew Lindstrom and Mark Strynar) stop by on Monday (8/18) to collect a few water samples for 1,4-dioxane and polyfluorinated ether analyses?

We would like to sample:

Sweeney raw

Raw ozone effluent

Settled water

Settled water ozone effluent

BAC effluent

UV effluent

Finished water

ASR sample if such a sample can be pulled from the well

If possible, they would also like to sample Pender Co. Can you send me Brandon's phone #?

Rachel Ingham has contacted you as well as she is interested such data for her AWWA policy research. We can use the samples both for Rachel's purposes and for the Urban Water Consortium 1,4-dioxane project.

Looking ahead, will you be able to provide us with composited daily raw water samples over a period of 1-2 months again for the UWC project so we can assess variability in 1,4-dioxane levels in the river? In addition, weekly grab samples of raw and finished water, if possible.

On another note, we were invited by WRRRI to submit a full proposal for the ASR research we discussed in May. I will go ahead and develop the full proposal, which is due 8/25. One question: Have you drilled additional monitoring wells already, or is that still in the future. In either case, I could use the following info:
1. distances of new monitoring wells from the ASR well 2. was/will PeeDee aquifer core samples be kept that we can use to conduct microcosm experiments?

We can talk by phone about all of this if you like.

Best,
Detlef

Best,
Detlef

On 6/24/14 10:39 AM, Tiffanie Hawley wrote:
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>

> I did hear back from Brandon Garner at Pender Co, and he is interested in a meeting here at Sweeney to hear you explain the research, but I haven't heard from Glenn Walker at Brunswick yet...

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> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Thursday, June 19, 2014 11:35 AM

> To: Michael Richardson; Tiffanie Hawley

> Subject: Sampling for polyfluorinated ethers

>

> Mike and Tiffany,

> It was good to see you yesterday... Can you send me contact info for the Brunswick Co. and Pender Co. plants?

> Thank you,

> Detlef

>

> --

> Detlef Knappe

> Professor

> 319-E Mann Hall

> Department of Civil, Construction, and Environmental Engineering North

> Carolina State University Campus Box 7908 Raleigh, NC 27695-7908

>

> Phone: 919-515-8791

> Fax: 919-515-7908

> E-mail: knappe@ncsu.edu

> Web page: <http://www4.ncsu.edu/~knappe>

>

--

Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://www4.ncsu.edu/~knappe>

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Monday, August 18, 2014 9:55 AM
To: Tiffanie Hawley; Michael Richardson
Subject: Re: Sampling for polyfluorinated ethers

Sample Event!

Hi Tiffanie,
The sampling crew is planning to arrive at 10.
Ok to sample raw ozone effluent after chemical addition.
Post-UV better before chemical addition
Finished water = POE.
If there are questions, please call 919-274-7307.
Thank you,
Detlef

On 8/15/14 5:26 PM, Tiffanie Hawley wrote:

> Going back to your original message, I wanted to point out a few
> things, so please see notes below with ****

>
>
>

> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]
> Sent: Wednesday, August 13, 2014 10:58 AM
> To: Tiffanie Hawley; Michael Richardson
> Subject: Re: Sampling for polyfluorinated ethers

>

> Hi Tiffany and Mike,

>

> Can my post-doc (Mei Sun) and two EPA researchers (Andrew Lindstrom and Mark Strynar) stop by on Monday (8/18)
to collect a few water samples for 1,4-dioxane and polyfluorinated ether analyses?

>

> We would like to sample:

> Sweeney raw

> Raw ozone effluent ****We do not have a way to sample raw ozone effluent before any chemical addition. The
only way to do this is to remove hatches from the preozonation contactors, which allows
offgassed ozone to release to atmosphere and puts the sampler in danger of inhalation.

> Settled water

> Settled water ozone effluent ****We refer to this as Filter Influent Flume, fyi

> BAC effluent

> UV effluent **** Do you want UV effluent before or after chemical addition?

> Finished water ****I assume you are referring to Entry Point?

> ASR sample if such a sample can be pulled from the well

>

> If possible, they would also like to sample Pender Co. Can you send me Brandon's phone #?
3637

>

****(910) 663-

> Rachel Ingham has contacted you as well as she is interested such data for her AWWA policy research. We can use the
samples both for Rachel's purposes and for the Urban Water Consortium 1,4-dioxane project.

>

> Looking ahead, will you be able to provide us with composited daily raw water samples over a period of 1-2 months again for the UWC project so we can assess variability in 1,4-dioxane levels in the river? In addition, weekly grab samples of raw and finished water, if possible. ****I will check with the compliance division to borrow their composite sampler again.

>

> On another note, we were invited by WRRRI to submit a full proposal for the ASR research we discussed in May. I will go ahead and develop the full proposal, which is due 8/25. One question: Have you drilled additional monitoring wells already, or is that still in the future. In either case, I could use the following info:

> 1. distances of new monitoring wells from the ASR well 2. was/will PeeDee aquifer core samples be kept that we can use to conduct microcosm experiments?

>

> ***** The new monitoring wells are in, but I am not sure about the core samples - that would be a question for Gary McSmith or John Malone with CFPUA.

>

> We can talk by phone about all of this if you like.

>

> Best,

> Detlef

>

> Best,

> Detlef

>

>

>

> On 6/24/14 10:39 AM, Tiffanie Hawley wrote:

>> Detlef, I didn't see where I responded to you last week - my bad.

>>

>> I did hear back from Brandon Garner at Pender Co, and he is interested in a meeting here at Sweeney to hear you explain the research, but I haven't heard from Glenn Walker at Brunswick yet...

>>

>> -----Original Message-----

>> From: Detlef Knappe [mailto:knappe@ncsu.edu]

>> Sent: Thursday, June 19, 2014 11:35 AM

>> To: Michael Richardson; Tiffanie Hawley

>> Subject: Sampling for polyfluorinated ethers

>>

>> Mike and Tiffany,

>> It was good to see you yesterday... Can you send me contact info for the Brunswick Co. and Pender Co. plants?

>> Thank you,

>> Detlef

>>

>> --

>> Detlef Knappe

>> Professor

>> 319-E Mann Hall

>> Department of Civil, Construction, and Environmental Engineering

>> North Carolina State University Campus Box 7908 Raleigh, NC

>> 27695-7908

>>

>> Phone: 919-515-8791

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Web page: <http://www4.ncsu.edu/~knappe>

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Monday, October 13, 2014 11:09 AM
To: Michael Richardson
Subject: NSF proposal
Attachments: Mapping NSF GOALIE proposal.docx

Mike,

I would like to explore with you the opportunity to write a proposal to NSF to study the occurrence of fluorochemicals in the Cape Fear River and to assess/develop treatment options. NSF has a program called GOALIE, that is designed to encourage collaboration between universities and industry. I was at NSF last week, and they were excited about the proposal idea. I would like to go ahead and develop a full proposal to this program (Nov. 5 deadline). To accomplish this, I would like to add you as a co-principal investigator. I have a similar, but smaller GOALIE project right now for 1,4-dioxane, on which Chad Ham is a co-PI. Attached is an outline of what I have in mind. Let's chat by phone to explore further. When is a good time for you?

Best,
Detlef

--
Detlef Knappe
Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Draft Map of NSF GOALIE proposal

Questions/Hypotheses	Limitations/Knowledge Gaps	Addressing knowledge gaps
<p>1. What is the total organic fluorine concentration in drinking water sources?</p> <p>2. What are the principal organic fluorine species contributing the total organic fluorine concentration?</p> <p>3. Hypothesis: Recently discovered polyfluorinated ethers dominate the total organic fluorine concentrations downstream of fluorochromal production facilities.</p>	<ul style="list-style-type: none"> No published information exists about the occurrence of polyfluorinated ethers in the aquatic environment Limited information is available about the identity of fluorochromals contributing to the adsorbable organic fluorine concentration. 	<p>Hypothesis 1: Recently discovered polyfluorinated ethers dominate the total organic fluorine concentrations downstream of fluorochromal production facilities (support hypothesis with preliminary data we have collected).</p> <p>Objective 1: Develop total organic fluorine assay.</p> <p>Objective 2: Develop quantitative LC-MS/MS method for polyfluorinated ethers</p> <p>Objective 3: Determine total organic fluorine concentrations and polyfluorinated ether concentrations as well as perfluorinated carboxylic acid and sulfonic acid concentrations in Cape Fear River water.</p> <p>Expected Outcomes:</p> <ul style="list-style-type: none"> New analytical method for emerging fluorochromals Development/refinement of analytical tools to close the mass balance on highly-fluorinated compounds [AOF assay, non-target analysis (HRMS), targeted analysis (LC-MS/MS)] Identification of fluorochromal signatures in surface water downstream of a fluorochromal production facility Mass flows of fluorochromals Variability in fluorochromal concentrations as a function of stream flow Manuscript describing analytical method for total organic fluorine and polyfluorinated ethers and application of methods to characterize fluorochromal signature and concentrations in a drinking water source. <p>Expected Benefits:</p> <ul style="list-style-type: none"> Comprehensive assessment methodology for fluorochromal occurrence in drinking water sources Graduate students in environmental engineering cross trained in analytical methods Involvement of undergraduates in summer research opportunities at NC State, the Cape Fear Public Utilities Commission, and USEPA <p>Outreach Opportunities:</p> <ul style="list-style-type: none"> Inform drinking water providers and wastewater utilities about a new class of fluorochromals Introduce emerging industrial pollutants to state and federal regulators (NC Public Water Supply Section, NPDES Permit Section, and USEPA) Outreach to stakeholders (e.g. Cape Fear River Assembly) Inform the public about emerging industrial pollutants (e.g. Rotary Club)

Question/Hypothesis	Limitations/Knowledge Gaps	Renewal: Addressing data gaps
<p>4. What treatment approaches can effectively remove/transform polyfluorinated ethers?</p> <p>5. Hypothesis: Polyfluorinated ethers are not readily controlled with incumbent water treatment technologies (polyfluorinated ethers do not contain functional groups that readily react with ozone and hydroxyl radicals, inclusion of ether linkages increases aqueous solubility and decreases adsorbability). Corollary: New treatment processes need to be developed for effective fluorochemical control.</p>	<ul style="list-style-type: none"> • No published water treatment information exists for polyfluorinated ethers 	<p>Hypothesis 2: Incumbent water treatment technologies do not effectively remove/transform polyfluorinated ethers (supporting preliminary data: no measurable oxidative transformation with ozone, no transformation during biological filtration, poorly adsorbed by activated carbon).</p> <p>Hypothesis 3: Tailored sorbents (aminated carbon) and emerging advanced oxidation processes (UV-activated peroxysulfate/peroxydisulfate) may offer cost- and energy-effective opportunities for polyfluorinated ether removal/transformation</p> <p>Objective 4: Quantify polyfluorinated ether removal/transformation in full-scale water treatment and aquifer storage and recovery systems</p> <p>Objective 5: Determine the effectiveness of incumbent and new physical removal processes (activated carbon, tailored activated carbon, ion exchange)</p> <p>Objective 6: Determine the effectiveness of incumbent and new advanced oxidation processes for the transformation of polyfluorinated ethers (ozonation, UV/H₂O₂, UV/peroxysulfate, UV/peroxydisulfate)</p> <p>Objective 7: Assess the capacity of known ether-degrading microorganisms to degrade polyfluorinated ethers</p> <p>Expected Outcomes:</p> <ul style="list-style-type: none"> • Identify/develop effective treatment processes for the control of polyfluorinated ethers • Close the fluorine mass balance for redox and biological transformation processes (AOF assay, non-target analysis (HRMS), targeted analysis (LC-MS/MS)) • Manuscripts describing treatment strategies for polyfluorinated ethers <p>Expected Benefits:</p> <ul style="list-style-type: none"> • Potential to develop new water treatment processes for industrial dischargers and drinking water utilities • Potential to close total fluorine mass balance in both raw water and during treatment <p>Outreach Opportunities:</p> <ul style="list-style-type: none"> • Outreach to stakeholders (e.g. Cape Fear River Assembly) • On-site training of graduate students at a state-of-the-art water treatment facility and on-site training of water treatment staff in emerging analytical chemistry methods

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Thursday, October 30, 2014 10:59 PM
To: Michael Richardson
Subject: Re: NSF
Attachments: NSF Goalie support letter - 30-OCT-14.docx

Mike,

Please see edits in the attached letter. Would it be possible to link your NC Warn chairmanship to planned outreach activities?
Detlef

On 10/30/14 2:59 PM, Michael Richardson wrote:

> documents

>

> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Tuesday, October 28, 2014 9:49 AM

> To: Michael Richardson

> Subject: NSF

>

> Good morning, Mike.

> How are things coming along with the NSF docs? Can you send me drafts by COB tomorrow?

> Most important pieces:

> 1. Letter (include [1] collaborative elements - host student to become familiar with advanced water treatment processes and ASR, study fate of perfluorinated(poly)ethers (PFPEs) in full-scale unit processes as well as during ASR and [2] ways you would like to contribute, especially with respect to communicating results to stakeholders) 2. Your resume - I can put it into the proper format.

>

> Here are a few points from the proposal guide that may help guide what to include in your letter:

>

> Opportunities are made available for collaborative industry-university projects for individuals or small groups. These research and education projects are jointly designed and implemented by university and industry engineers and scientists. The principal investigators and their students are encouraged to perform some of their research at the industrial sites. Researchers from industry and academe tend to complement each other and thus form effective teams. Many teams provide expertise in materials, devices, characterization, measurements, or other areas that exceed the capabilities of a single group. This mechanism offers a special opportunity for industry, including small businesses, to leverage their research efforts with university research in collaborative projects.

>

> Proposal description: The proposal must describe the research approach and a detailed plan of the industry-university collaboration including the tasks for both partners. The purpose of the eventual visit(s) in industry or academe must be explained. In the last year of the project, the principal investigator must plan at least two industrial seminars, one of which should be within the collaborating industrial unit. GOALI research projects must demonstrate measurable industry collaboration and involvement that accelerates fundamental research.

>

> Let me know if you would like to talk.

> Thank you,

> Detlef

>

> --
> Detlef Knappe
> Professor
> 319-E Mann Hall
> Department of Civil, Construction, and Environmental Engineering North
> Carolina State University Campus Box 7908 Raleigh, NC 27695-7908
>
> Phone: 919-515-8791
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319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
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James R. Flechtner, PE
Executive Director
235 Government Center Drive
Wilmington, NC 28403
910-332-6542
jim.flechtner@cfpua.org

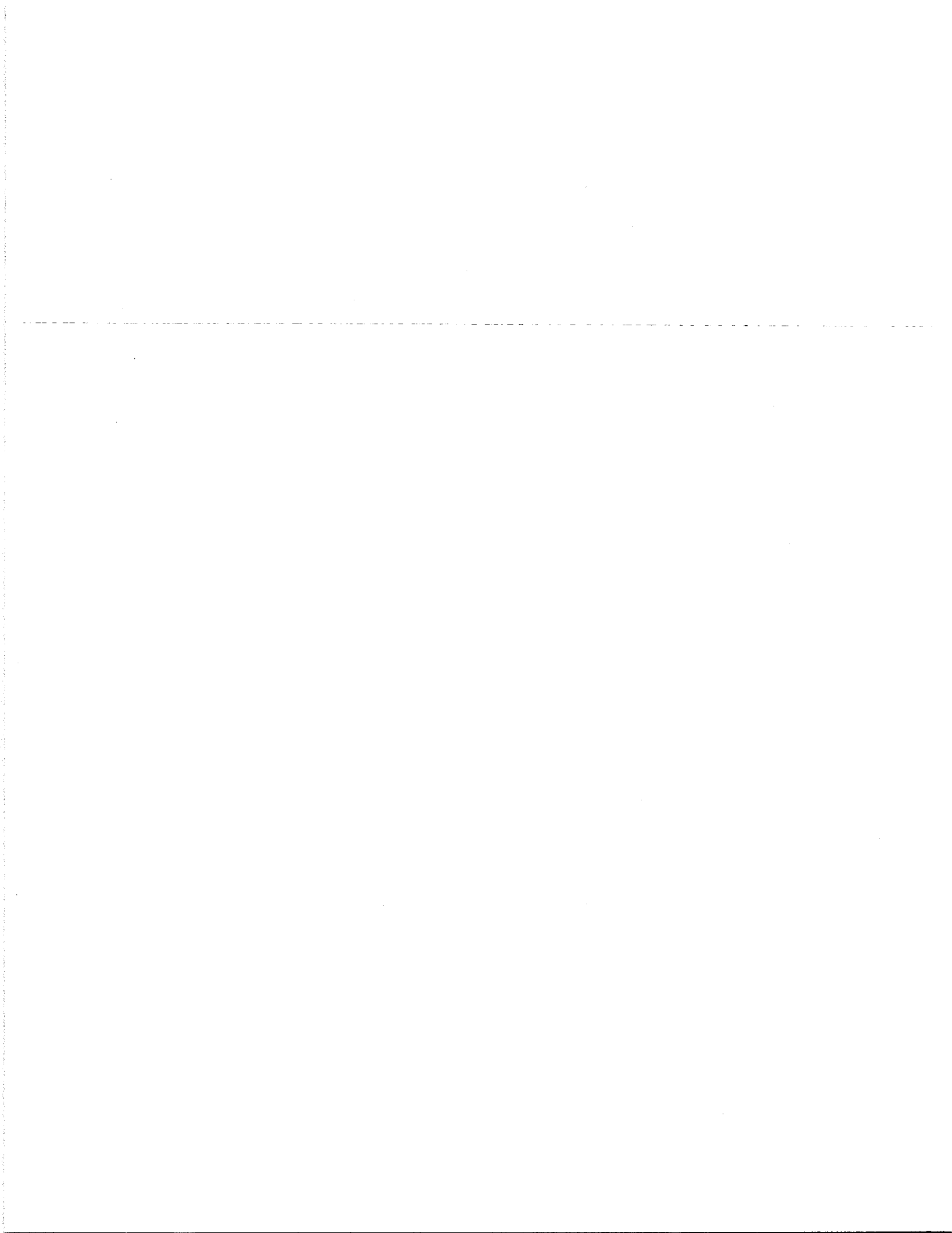
June 7, 2017

Ms. Sheila Holman
State of North Carolina
Department of Environmental Quality
Assistant Secretary for Environment
1601 Mail Service Center
Raleigh, North Carolina 27699-1601

Dear Ms. Holman:

Cape Fear Public Utility Authority provides water and sewer service to nearly 200,000 customers in New Hanover County and the City of Wilmington. In addition to obtaining raw water from groundwater sources, the Authority uses surface water from the Cape Fear River, just upstream of Lock & Dam # 1 in Bladen County for treatment at the Sweeney Water Treatment Plant and distribution to customers. The Sweeney Water Treatment Plant uses advanced treatment processes such as advanced coagulation/flocculation/sedimentation, ozone and UV, and BAC filtration.

Recent research through N. C. State University shows that, since the year 2000 per and poly-fluoroalkyl substances have been introduced onto the market to replace long chain perfluoroalkyl acids (e.g. perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) and their respective precursors). This research indicates these poly-fluoroalkyl substances are present in the Lower Cape Fear River source water. These compounds are currently not regulated at the state or federal levels for discharge into the river. Due to the persistence of these compounds and the ineffectiveness of existing water treatment technologies in removing these compounds, these substances should be regulated at the point of discharge into the river to ensure they do not compromise public water supplies.

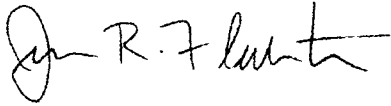


June 7, 2017

Page Two

Enclosed is a publication titled "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminates in the Cape Fear River Watershed of North Carolina" for your reference. As this is newly available information, we would welcome your assistance in evaluating implications for the area's source water. We would support actions identified by NCDEQ to ensure proper regulation and management of the dischargers for the protection of the river and its users. If additional information or assistance is needed, please contact me.

Sincerely,

A handwritten signature in black ink, appearing to read "Jim R. Flechtner". The signature is fluid and cursive, with a long horizontal stroke at the end.

James R. Flechtner, PE
Executive Director

Copy: Jay Zimmerman, Director NCDWR
Julie Grzyb, NPDES Permitting Supervisor
Jessica Godreau, PWS Section Chief

Enclosure

Beth Eckert

From: Gregson, Jim <jim.gregson@ncdenr.gov>
Sent: Thursday, June 8, 2017 1:53 PM
To: Beth Eckert
Subject: FW: renewal

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section
Division of Water Resources
Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
Jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405

*Email correspondence to and from this address is subject to the
North Carolina Public Records Law and may be disclosed to third parties.*

From: Chernikov, Sergei
Sent: Thursday, June 08, 2017 1:44 PM
To: Gregson, Jim <jim.gregson@ncdenr.gov>
Subject: renewal

Jim,

You can download the renewal application from this site:

<http://edocs.deq.nc.gov/WaterResources/0/doc/482844/Page1.aspx>

Thank you!

Sergei

Sergei Chernikov, Ph.D.
Environmental Engineer II
Complex NPDES Permitting Unit

Tel. 919-807-6386

Fax: 919-807-6489

1617 Mail Service Center, Raleigh, NC 27699-1617

Express Mail: 512 N. Salisbury St., Raleigh, NC 27604



**Evaluation of substances used in the GenX
technology by Chemours, Dordrecht**

RIVM Letter report 2016-0174
M. Beekman et al.



National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

**Evaluation of substances used in the GenX
technology by Chemours, Dordrecht**

RIVM Letter report 2016-0174
M. Beekman et al.



Dr. Detlef Knappe
North Carolina State University
Department of Civil, Construction, and Environmental Engineering
Campus Box 7908
Raleigh, NC 27695-7908

October 30, 2014

Re: GOALI: Perfluoro(poly)ethers - an emerging class of drinking water contaminants

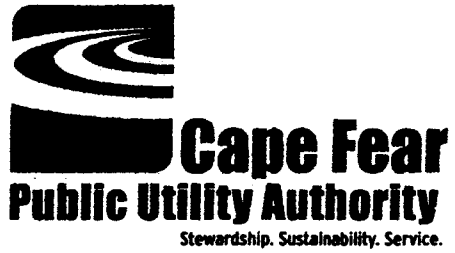
Dear Dr. Knappe,

The purpose of this letter is to confirm that the Cape Fear Public Utility Authority (CFPUA) has a strong interest in collaborating with you and your students on the above referenced research. In my position as the Water Resources Manager at CFPUA, I confirm my participation as a co-principal investigator. CFPUA's Sweeney water treatment plant (WTP) has a design capacity of 35 mgd and treats water from the Cape Fear River. Apart from conventional water treatment processes, our treatment train includes both raw and settled water ozonation, granular activated carbon (GAC) biofiltration, and UV disinfection. Even with these advanced treatment processes, our results from ongoing sampling for USEPA's third unregulated contaminant monitoring rule (UCMR3) show that unregulated contaminants such as 1,4-dioxane and perfluoroalkyl substances PFASs occur in our finished water. In addition, analyses conducted by you and your colleagues at EPA identified new perfluoro(poly)ethers (PFPEs) in the raw and finished water from the Sweeney WTP. CFPUA is concerned about the presence of PFPEs and other unregulated industrial contaminants in our source water, especially because many respond either poorly or not at all to the advanced treatment processes available at the Sweeney WTP. An additional concern of ours is the fate of PFPEs in our aquifer storage and recovery (ASR) system. CFPUA would like to partner with you to (1) develop analytical methods that will allow us to quantify PFPE concentrations in our source water, (2) measure adsorbable organic fluorine (AOF) to determine what fraction of the AOF is identifiable by targeted LC-MS/MS analysis, (3) assess PFPE removal/transformation in the treatment processes employed at the Sweeney WTP and in our ASR facility, and (4) identify treatment options for PFPE removal from water.

Some ways in which CFPUA will contribute to the proposed research are as follows:

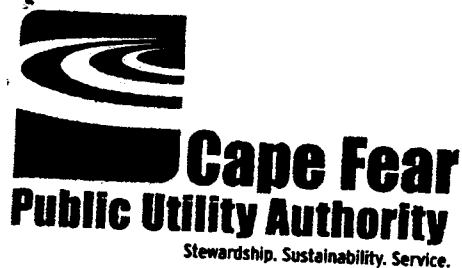
- Host student to become familiar with advanced water treatment processes used at Sweeney WTP and at our ASR facility
- Closely collaborate with you and your student to study the removal/transformation of PFPEs in full-scale unit processes as well as during ASR.
- Work with you to communicate the results of the study to affected utilities and coordinate efforts between affected utilities, regulatory agencies, and identified sources to eliminate and /or reduce PFPE concentrations in the Cape Fear River to acceptable levels.

Our goal is to closely collaborate with you and your graduate students to facilitate knowledge transfer. If you have any questions, feel free to contact me by email at Michael.richardson@cfpua.org or by phone at 910-332-6723.



Sincerely,

Michael Richardson
Water Resources Manager



Dr. Detlef Knappe
North Carolina State University
Department of Civil, Construction, and Environmental Engineering,
Campus Box 7908
Raleigh, NC 27695-7908

October 30, 2014

Re: ~~RAPID~~ GOALIE: Perfluoro(poly)ethers - an emerging class of drinking water contaminants ~~GOALIE - Study of Occurrence of Fluorochemicals in the Cape Fear River to Assess/Develop Treatment Options~~

Dear Dr. Knappe,

The purpose of this letter is to confirm that the Cape Fear Public Utility Authority (CFPUA) has a strong interest in collaborating with you and your students on the above referenced research. In my position as the Water Resources Manager at CFPUA, I confirm my participation as a co-principal investigator. CFPUA's Sweeney water treatment plant (WTP) operates a surface water treatment plant (Sweeney WTP - 35 MGD) that has a design capacity of 35 mgd and use treats water from the Cape Fear River. Apart from conventional water treatment processes, our treatment train includes both raw and settled water ozonation, granular activated carbon (GAC) biofiltration, and UV disinfection. Even with these advanced treatment processes, our results from ongoing sampling for USEPA's third unregulated contaminant monitoring rule (UCMR3) show that unregulated contaminants such as 1,4-dioxane and perfluoroalkyl substances PFASs occur in our finished water. In addition, analyses conducted by you and your colleagues at EPA We have found identified new elevated levels of Fluorochemicals perfluoro(poly)ethers (PFPEs) in the raw and finished water from the this facility Sweeney WTP. CFPUA is concerned about the presence of PFPEs and other unregulated industrial contaminants in our source water, especially because many respond either poorly or not at all to the advanced treatment processes available at the Sweeney WTP. An additional concern of ours is the fate of PFPEs in our aquifer storage and recovery (ASR) system. CFPUA would like to partner with you to (1) develop analytical methods that will allow us to quantify PFPE concentrations in our source water, (2) measure adsorbable organic fluorine (AOF) to determine what fraction of the AOF is identifiable by targeted LC-MS/MS analysis, (3) assess PFPE removal/transformation in the treatment processes employed at the Sweeney WTP and in our ASR facility, and (4) identify treatment options for PFPE removal from water.

Some ways in which CFPUA will contribute to the proposed research are as follows:

- Host students to become familiar with advanced water treatment processes used at Sweeney WTP and at our ASR Facility
- Closely collaborate with you and your student to study the fate removal/transformation of Perfluorinated (poly)ethers (PFPEs) in full-scale unit processes as well as during ASR recovery.
- Interact closely with you and your students to assure that fundamental knowledge developed in the proposed research results in actionable data and information that is relevant to CFPUA as well as other drinking water providers that face challenges associated with Fluorochemicals in their source water.
- Work with you to communicate the results of the study to affected utilities and coordinate efforts between affected utilities, regulatory agencies, and identified sources to eliminate and /or reduce ~~Fluorochemicals~~ PFPE concentrations in the Cape Fear River to acceptable levels.

235 Government Center Drive, Wilmington, NC 28403
t: 910-799-6064 f: 910-799-6066 www.cfpu.org



Cape Fear Public Utility Authority

Stewardship. Sustainability. Service.

Our goal is to closely collaborate with you and your graduate students to facilitate knowledge transfer. If you have any questions, feel free to contact me by email at Michael.richardson@cfpua.org or by phone at 910-332-6723.

Sincerely,

**Michael Richardson
Water Resources Manager**

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Friday, October 31, 2014 12:13 PM
To: Michael Richardson
Subject: Re: NSF

yep... i looked up the NC Water Warn web site this morning :)

for your CV, can you send me:

1. conference presentations
2. example instructor activities?

For the student hosting, would you be willing to host a student for a couple of months so that student can learn about different aspects of CFPUA systems (e.g. process operations at Sweeney, ASR operation, water quality analysis and aspects of regulatory compliance)? Student would be paid from the grant. Procedurally, would it be possible for a student to essentially be an intern at CFPUA and be teamed up with different people to learn about the different aspects of drinking water treatment and ASR? Part of the student's time at CFPUA could be used to (1) set up and run a small GAC pilot to obtain PFPE breakthrough curves, (2) collect full-scale samples at Sweeney, and (3) collect ASR samples. Let me know if you have other ideas. The student would likely be my PhD student Zachary Hopkins.

Also, what do you think are the best avenues for communicating results?

If you could briefly outline how you think results from this research could be most effectively communicated using the networks you have, it would be great.

Thank you,
Detlef

On 10/31/14 11:59 AM, Michael Richardson wrote:

> OK with the proposed changes to the letter.

>

> NCWaterWARN: not sure that it is relevant as WARN is a mutual aid response network offering to assist other members and utilities with equipment, material, and personnel during times of emergency need or disasters.

>

> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Thursday, October 30, 2014 10:59 PM

> To: Michael Richardson

> Subject: Re: NSF

>

> Mike,

> Please see edits in the attached letter. Would it be possible to link your NC Warn chairmanship to planned outreach activities?

> Detlef

>

> On 10/30/14 2:59 PM, Michael Richardson wrote:

>> documents

>>

>> -----Original Message-----

>> From: Detlef Knappe [mailto:knappe@ncsu.edu]
>> Sent: Tuesday, October 28, 2014 9:49 AM
>> To: Michael Richardson
>> Subject: NSF
>>
>> Good morning, Mike.
>> How are things coming along with the NSF docs? Can you send me drafts by COB tomorrow?
>> Most important pieces:
>> 1. Letter (include [1] collaborative elements - host student to become familiar with advanced water treatment processes and ASR, study fate of perfluorinated(poly)ethers (PFPEs) in full-scale unit processes as well as during ASR and [2] ways you would like to contribute, especially with respect to communicating results to stakeholders) 2. Your resume - I can put it into the proper format.
>>
>> Here are a few points from the proposal guide that may help guide what to include in your letter:
>>
>> Opportunities are made available for collaborative industry-university projects for individuals or small groups. These research and education projects are jointly designed and implemented by university and industry engineers and scientists. The principal investigators and their students are encouraged to perform some of their research at the industrial sites. Researchers from industry and academe tend to complement each other and thus form effective teams. Many teams provide expertise in materials, devices, characterization, measurements, or other areas that exceed the capabilities of a single group. This mechanism offers a special opportunity for industry, including small businesses, to leverage their research efforts with university research in collaborative projects.
>>
>> Proposal description: The proposal must describe the research approach and a detailed plan of the industry-university collaboration including the tasks for both partners. The purpose of the eventual visit(s) in industry or academe must be explained. In the last year of the project, the principal investigator must plan at least two industrial seminars, one of which should be within the collaborating industrial unit. GOALI research projects must demonstrate measurable industry collaboration and involvement that accelerates fundamental research.
>>
>> Let me know if you would like to talk.
>> Thank you,
>> Detlef
>>
>> --
>> Detlef Knappe
>> Professor
>> 319-E Mann Hall
>> Department of Civil, Construction, and Environmental Engineering
>> North Carolina State University Campus Box 7908 Raleigh, NC
>> 27695-7908
>>
>> Phone: 919-515-8791
>> Fax: 919-515-7908
>> E-mail: knappe@ncsu.edu
>> Web page: <http://knappelab.wordpress.ncsu.edu/>
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100

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Tuesday, November 04, 2014 2:53 PM
To: Michael Richardson
Subject: Re: NSF
Attachments: Michael Ennis Richardson-NSF 30-OCT-14.docx

Mike,

I googled around a bit and found a few conference presentations online.

I updated your CV by adding the presentations and by adding your Fuller award (attached). If you can send me info on one or two more presentation - perhaps dealing with ozone, UV, GAC biofiltration, it would be great. You can just send me the presentation file and let me know when and where you presented.

Thank you for the other pointers!

Detlef

On 11/4/14 12:59 PM, Michael Richardson wrote:

> I cannot find my listing of presentations. For the last few years my presentations have been about NCWaterWARN and the Value of Membership to the water and wastewater systems of the state. I have also presented about our ASR Program and its' incorporation into our current water system. I have also presented on the overall creation of CFPWA and how we are operated and governed. Prior years I have made several presentations about our ozone system and how we comply through the use of ozone and free chlorine.

>

> I have not taught for many several years now. I have instructed operators in maintenance, residual solids, safety coagulation/filtration, disinfection and general operation of water treatment plants.

>

> I would honored to host a student and to mentor to that student about our unique approaches to water treatment. We can certainly assist with the GAC pilot and all the necessary sampling and related work needed.

>

> I would propose using our connection through the Urban Water Consortium as a great avenue to disseminate the information, the fact that we are a subscriber to WRF, and would try to present at NCWOA meets and seminars. I would also like to present at both the Spring Conference and the Annual Conference for NCAWWA-WEA to continue to spread the word.

>

> Hope this helps. Sorry but I am really slammed with work due to budget and project meeting and do not have any spare time for the next few days. Please just send me email and I will try to reply as soon as possible.

>

>

> -----Original Message-----

> From: Detlef Knappe [mailto:knappe@ncsu.edu]

> Sent: Monday, November 03, 2014 2:06 PM

> To: Michael Richardson

> Subject: Re: NSF

>

> Mike,

> Proposal is due Wed :) do you have time for a quick phone call tomorrow?

>

> Also

>

> for your CV, can you send me:

> 1. conference presentations
> 2. example instructor activities?
>
> For the student hosting, would you be willing to host a student for a couple of months so that student can learn about different aspects of CFPUA systems (e.g. process operations at Sweeney, ASR operation, water quality analysis and aspects of regulatory compliance)? Student would be paid from the grant. Procedurally, would it be possible for a student to essentially be an intern at CFPUA and be teamed up with different people to learn about the different aspects of drinking water treatment and ASR? Part of the student's time at CFPUA could be used to (1) set up and run a small GAC pilot to obtain PFPE breakthrough curves, (2) collect full-scale samples at Sweeney, and (3) collect ASR samples. Let me know if you have other ideas. The student would likely be my PhD student Zachary Hopkins.
>
> Also, what do you think are the best avenues for communicating results?
> If you could briefly outline how you think results from this research could be most effectively communicated using the networks you have, it would be great.
>
> Thank you,
> Detlef
>
>
> On 10/31/14 11:59 AM, Michael Richardson wrote:
>> OK with the proposed changes to the letter.
>>
>> NCWaterWARN: not sure that it is relevant as WARN is a mutual aid response network offering to assist other members and utilities with equipment, material, and personnel during times of emergency need or disasters.
>>
>> -----Original Message-----
>> From: Detlef Knappe [mailto:knappe@ncsu.edu]
>> Sent: Thursday, October 30, 2014 10:59 PM
>> To: Michael Richardson
>> Subject: Re: NSF
>>
>> Mike,
>> Please see edits in the attached letter. Would it be possible to link your NC Warn chairmanship to planned outreach activities?
>> Detlef
>>
>> On 10/30/14 2:59 PM, Michael Richardson wrote:
>>> documents
>>>
>>> -----Original Message-----
>>> From: Detlef Knappe [mailto:knappe@ncsu.edu]
>>> Sent: Tuesday, October 28, 2014 9:49 AM
>>> To: Michael Richardson
>>> Subject: NSF
>>>
>>> Good morning, Mike.
>>> How are things coming along with the NSF docs? Can you send me drafts by COB tomorrow?
>>> Most important pieces:
>>> 1. Letter (include [1] collaborative elements - host student to become familiar with advanced water treatment processes and ASR, study fate of perfluorinated(poly)ethers (PFPEs) in full-scale unit processes as well as during ASR and [2] ways you would like to contribute, especially with respect to communicating results to stakeholders) 2. Your resume - I can put it into the proper format.

>>>

>>> Here are a few points from the proposal guide that may help guide what to include in your letter:

>>>

>>> Opportunities are made available for collaborative industry-university projects for individuals or small groups. These research and education projects are jointly designed and implemented by university and industry engineers and scientists. The principal investigators and their students are encouraged to perform some of their research at the industrial sites. Researchers from industry and academe tend to complement each other and thus form effective teams. Many teams provide expertise in materials, devices, characterization, measurements, or other areas that exceed the capabilities of a single group. This mechanism offers a special opportunity for industry, including small businesses, to leverage their research efforts with university research in collaborative projects.

>>>

>>> Proposal description: The proposal must describe the research approach and a detailed plan of the industry-university collaboration including the tasks for both partners. The purpose of the eventual visit(s) in industry or academe must be explained. In the last year of the project, the principal investigator must plan at least two industrial seminars, one of which should be within the collaborating industrial unit. GOALI research projects must demonstrate measurable industry collaboration and involvement that accelerates fundamental research.

>>>

>>> Let me know if you would like to talk.

>>> Thank you,

>>> Detlef

>>>

>>> --

>>> Detlef Knappe

>>> Professor

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Web page: <http://knappelab.wordpress.ncsu.edu/>

Michael Ennis Richardson
Cape Fear Public Utility Authority
Wilmington, NC

Professional Preparation

Fayetteville Technical Institute, Fayetteville, NC Environmental Engineering Technology A.S., 1975

Appointments

2008 – present	Water Resources Manager, Cape Fear Public Utility Authority, Wilmington, NC
1994 – 2008	Water Treatment Superintendent, City of Wilmington, Wilmington, NC
1991 – 1994	Manager, Cleveland County Sanitary District, Lawndale, NC
1981 – 1991	Superintendent, Montgomery County Water System, Troy, NC
1980 – 1981	Technical Specialist, NC Rural Water Association, Welcome, NC
1978 – 1980	Chief Operator, NE Metropolitan Water, Lillington, NC
1976 – 1978	Asst Public Works Director, Town of Lillington, NC

Representative Conference Presentations

Richardson, M.E. and T. 2013. CFPUA: Water resources for the future. NCAWWA Spring Conference, Wilmington, NC.

Richardson, M.E., Johnson, N. and Derr, A. 2013. Meeting the challenges of upgrading the plant control system yields major operations benefits. NCAWWA Annual Conference, Concord, NC.

Richardson, M.E. 2012. Drinking Water Sources – Taste & Odor Plus?? North Carolina Forum on Nutrient Over-Enrichment, Durham, NC.

Coggins, J. and Richardson, M. 2010. Phased approach to constructing the expansion of the Sweeney WTP. NCAWWA Spring Conference, Wilmington, NC.

Synergistic Activities

- NCWaterWARN, Chairman 2008 – present. N.C. Water WARN is a network of water utilities helping each other respond to and recover from emergencies. This organization of water systems works independently of state government to assist members during an emergency. The mission of WARN is to provide expedited access to specialized resources needed to respond to and recover from natural and human caused events that disrupt public and private drinking water and wastewater utilities.
- Board member and committee member NCWOA, 1981 – present; President 1994 – 95; Vice-Chairman 1992 – 94
- AWWA George Warren Fuller Award, 2010
- Instructor for various schools for NCWOA, NCAWWA-WEA for over 20 years
- Board of Trustees NCAWWA-WEA 1998 – 2005; Chairman 2004-05; Vice-Chair 2003 – 04;
- Board member of NC Rural Water Association, 1985 – 1991; President 1987 – 88

2

John Malone

From: Michael Richardson
Sent: Wednesday, August 26, 2015 10:58 AM
To: Jim Flechtner (jim.flechtner@cfpua.org)
Cc: Leslie Ogilvie
Subject: FW: NSF proposal
Attachments: FullProposal.pdf

*NSF
PROPOSAL*

Wanted to make you aware of request for your signature on a document being sent to you (probably FEDEX) relating to this project that Dr. Knappe and I (CFPUA) are doing research on. There is no \$\$ from us, only in-kind contribution for sampling, data, and returning shipping labor. The project has been awarded a grant according to Dr. Knappe, however this document that requires your signature is needed by Friday in order to comply to receive the funding.

The proposal is attached so you can have a good understanding of the project. Thank you for your time and assistance with this matter. Please contact me with any questions or you may also contact Dr. Knappe at 919-274-7307.

I will be out of the office tomorrow and Friday in New Bern attending a Water Summit. I will have my phone should you need to contact me.

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Wednesday, August 26, 2015 10:38 AM
To: Michael Richardson
Subject: NSF proposal

Mike,
Attached is the NSF proposal about to be funded. Please let me know if you have any questions.
Best,
Detlef

--
Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

**02 INFORMATION ABOUT PRINCIPAL INVESTIGATORS/PROJECT DIRECTORS(PI/PD) and
co-PRINCIPAL INVESTIGATORS/co-PROJECT DIRECTORS**

Submit only ONE copy of this form for each PI/PD and co-PI/PD identified on the proposal. The form(s) should be attached to the original proposal as specified in GPG Section II.C.a. Submission of this information is voluntary and is not a precondition of award. This information will not be disclosed to external peer reviewers. ***DO NOT INCLUDE THIS FORM WITH ANY OF THE OTHER COPIES OF YOUR PROPOSAL AS THIS MAY COMPROMISE THE CONFIDENTIALITY OF THE INFORMATION.***

PI/PD Name: Michael E Richardson

Gender: ☐ Male ☐ Female
Ethnicity: (Choose one response) ☐ Hispanic or Latino ☐ Not Hispanic or Latino

Race:
(Select one or more)
☐ American Indian or Alaska Native
☐ Asian
☐ Black or African American
☐ Native Hawaiian or Other Pacific Islander
☐ White

Disability Status:
(Select one or more)
☐ Hearing Impairment
☐ Visual Impairment
☐ Mobility/Orthopedic Impairment
☐ Other
☐ None

Citizenship: (Choose one) ☐ U.S. Citizen ☐ Permanent Resident ☐ Other non-U.S. Citizen

Check here if you do not wish to provide any or all of the above information (excluding PI/PD name): ☒

REQUIRED: Check here if you are currently serving (or have previously served) as a PI, co-PI or PD on any federally funded project ☐

Ethnicity Definition:

Hispanic or Latino. A person of Mexican, Puerto Rican, Cuban, South or Central American, or other Spanish culture or origin, regardless of race.

Race Definitions:

American Indian or Alaska Native. A person having origins in any of the original peoples of North and South America (including Central America), and who maintains tribal affiliation or community attachment.

Asian. A person having origins in any of the original peoples of the Far East, Southeast Asia, or the Indian subcontinent including, for example, Cambodia, China, India, Japan, Korea, Malaysia, Pakistan, the Philippine Islands, Thailand, and Vietnam.

Black or African American. A person having origins in any of the black racial groups of Africa.

Native Hawaiian or Other Pacific Islander. A person having origins in any of the original peoples of Hawaii, Guam, Samoa, or other Pacific Islands.

White. A person having origins in any of the original peoples of Europe, the Middle East, or North Africa.

WHY THIS INFORMATION IS BEING REQUESTED:

The Federal Government has a continuing commitment to monitor the operation of its review and award processes to identify and address any inequities based on gender, race, ethnicity, or disability of its proposed PIs/PDs. To gather information needed for this important task, the proposer should submit a single copy of this form for each identified PI/PD with each proposal. Submission of the requested information is voluntary and will not affect the organization's eligibility for an award. However, information not submitted will seriously undermine the statistical validity, and therefore the usefulness, of information received from others. Any individual not wishing to submit some or all the information should check the box provided for this purpose. (The exceptions are the PI/PD name and the information about prior Federal support, the last question above.)

Collection of this information is authorized by the NSF Act of 1950, as amended, 42 U.S.C. 1861, et seq. Demographic data allows NSF to gauge whether our programs and other opportunities in science and technology are fairly reaching and benefiting everyone regardless of demographic category; to ensure that those in under-represented groups have the same knowledge of and access to programs and other research and educational opportunities; and to assess involvement of international investigators in work supported by NSF. The information may be disclosed to government contractors, experts, volunteers and researchers to complete assigned work; and to other government agencies in order to coordinate and assess programs. The information may be added to the Reviewer file and used to select potential candidates to serve as peer reviewers or advisory committee members. See Systems of Records, NSF-50, "Principal Investigator/Proposal File and Associated Records", 63 Federal Register 267 (January 5, 1998), and NSF-51, "Reviewer/Proposal File and Associated Records", 63 Federal Register 268 (January 5, 1998).

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PI/PD Name: Detlef Knappe

Gender:

☒ Male

☐ Female

Ethnicity: (Choose one response)

☐ Hispanic or Latino ☒ Not Hispanic or Latino

Race:

(Select one or more)

☐ American Indian or Alaska Native
☐ Asian
☐ Black or African American
☐ Native Hawaiian or Other Pacific Islander
☒ White

Disability Status:

(Select one or more)

☐ Hearing Impairment
☐ Visual Impairment
☐ Mobility/Orthopedic Impairment
☐ Other
☒ None

Citizenship: (Choose one)

☒ U.S. Citizen ☐ Permanent Resident ☐ Other non-U.S. Citizen

Check here if you do not wish to provide any or all of the above information (excluding PI/PD name): ☐

REQUIRED: Check here if you are currently serving (or have previously served) as a PI, co-PI or PD on any federally funded project ☒

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Collection of this information is authorized by the NSF Act of 1950, as amended, 42 U.S.C. 1861, et seq. Demographic data allows NSF to gauge whether our programs and other opportunities in science and technology are fairly reaching and benefiting everyone regardless of demographic category; to ensure that those in under-represented groups have the same knowledge of and access to programs and other research and educational opportunities; and to assess involvement of international investigators in work supported by NSF. The information may be disclosed to government contractors, experts, volunteers and researchers to complete assigned work; and to other government agencies in order to coordinate and assess programs. The information may be added to the Reviewer file and used to select potential candidates to serve as peer reviewers or advisory committee members. See Systems of Records, NSF-50, "Principal Investigator/Proposal File and Associated Records", 63 Federal Register 267 (January 5, 1998), and NSF-51, "Reviewer/Proposal File and Associated Records", 63 Federal Register 268 (January 5, 1998).

Not Listed

COVER SHEET FOR PROPOSAL TO THE NATIONAL SCIENCE FOUNDATION

Not for distribution

PROGRAM ANNOUNCEMENT/SOLICITATION NO./CLOSING DATE/ If not in response to a program announcement/solicitation enter NSF 15-1		NSF 15-1		FOR CONSIDERATION BY NSF ORGANIZATION UNIT(S) (Indicate the most specific unit known, i.e., program, division, etc.)		CBET - Environmental Engineering					
DATE RECEIVED		NUMBER OF COPIES		DIVISION ASSIGNED		FUND CODE		DUNS# (Data Universal Numbering System)		FILE LOCATION	
								042092122			
EMPLOYER IDENTIFICATION NUMBER (EIN) OR TAXPAYER IDENTIFICATION NUMBER (TIN)		SHOW PREVIOUS AWARD NO. IF THIS IS		IS THIS PROPOSAL BEING SUBMITTED TO ANOTHER FEDERAL AGENCY? YES <input type="checkbox"/> NO <input checked="" type="checkbox"/> IF YES, LIST ACRONYM(S)		AN ACCOMPLISHMENT-BASED RENEWAL <input type="checkbox"/> A RENEWAL <input type="checkbox"/>					
566000756											
NAME OF ORGANIZATION TO WHICH AWARD SHOULD BE MADE		ADDRESS OF AWARD ORGANIZATION, INCLUDING 9 DIGIT ZIP CODE		CAMPUS BOX 7514 2701 Sullivan Drive, Suite 240 RALEIGH, NC 27695-7514		NAME OF PRIMARY PLACE OF PERF		North Carolina State University		0029728000	
AWARDEE ORGANIZATION CODE (if known)		ADDRESS OF PRIMARY PLACE OF PERF, INCLUDING 9 DIGIT ZIP CODE		North Carolina State University 2501 Stinson Dr. Raleigh, NC 276957908, US.		IS AWARDEE ORGANIZATION (Check All That Apply)		<input type="checkbox"/> SMALL BUSINESS <input type="checkbox"/> FOR-PROFIT ORGANIZATION <input type="checkbox"/> MINORITY BUSINESS <input type="checkbox"/> IF THIS IS A PRELIMINARY PROPOSAL THEN CHECK HERE		TITLE OF PROPOSED PROJECT EAGER: GOALIE: Perfluoro(poly)ethers - a new class of drinking water contaminants	
REQUESTED AMOUNT		PROPOSED DURATION (1-60 MONTHS)		REQUESTED STARTING DATE		SHOW RELATED PRELIMINARY PROPOSAL NO.					
\$ 89,849		12 months		08/15/15		IF APPLICABLE					
THIS PROPOSAL INCLUDES ANY OF THE ITEMS LISTED BELOW		<input type="checkbox"/> BEGINNING INVESTIGATOR (GPG I.G.2)		<input type="checkbox"/> DISCLOSURE OF LOBBYING ACTIVITIES (GPG II.C.1.e)		<input type="checkbox"/> PROPRIETARY & PRIVILEGED INFORMATION (GPG I.D. II.C.1.d)		<input type="checkbox"/> HISTORIC PLACES (GPG II.C.2.j)		<input type="checkbox"/> VERTEBRATE ANIMALS (GPG II.D.6) IACUC App. Date _____	
<input checked="" type="checkbox"/> FUNDING MECHANISM EAGER		<input checked="" type="checkbox"/> HUMAN SUBJECTS (GPG II.D.7) Human Subjects Assurance Number _____		Exemption Subsection _____ or IRB App. Date _____		<input type="checkbox"/> INTERNATIONAL ACTIVITIES: COUNTRY/COUNTRIES INVOLVED (GPG II.C.2.j)		<input checked="" type="checkbox"/> COLLABORATIVE STATUS		Not a collaborative proposal	
P/PD DEPARTMENT Civil, Construction, and Env Engineering		P/PD POSTAL ADDRESS NCSU Campus Box 7908 Dept. of Civil, Constr., and Env. Eng. Raleigh, NC 276957908 United States		P/PD NAME Dedert Knappe		P/PD FAX NUMBER 919-515-7908		P/PD DEPARTMENT Civil, Construction, and Env Engineering		P/PD POSTAL ADDRESS NCSU Campus Box 7908 Dept. of Civil, Constr., and Env. Eng. Raleigh, NC 276957908 United States	
P/PD NAME		High Degree		Yr of Degree		Telephone Number		Email Address			
CO-P/PI/D		P/D		1996		919-515-8791		knappe@ncsu.edu			
CO-P/PI/D		AS		1975		910-332-6723		michael.richardson@cfpna.org			
CO-P/PI/D											
CO-P/PI/D											
CO-P/PI/D											

CERTIFICATION PAGE

Certification for Authorized Organizational Representative (or Equivalent) or Individual Applicant

By electronically signing and submitting this proposal, the Authorized Organizational Representative (AOR) or Individual Applicant is: (1) certifying that statements made herein are true and complete to the best of his/her knowledge; and (2) agreeing to accept the obligation to comply with NSF award terms and conditions if an award is made as a result of this application. Further, the applicant is hereby providing certifications regarding conflict of interest (when applicable), drug-free workplace, debarment and suspension, lobbying activities (see below), nondiscrimination, flood hazard insurance (when applicable), responsible conduct of research, organizational support, Federal tax obligations, unpaid Federal tax liability, and criminal convictions as set forth in the NSF Proposal & Award Policies & Procedures Guide, Part I: the Grant Proposal Guide (GPG). Willful provision of false information in this application and its supporting documents or in reports required under an ensuing award is a criminal offense (U.S. Code, Title 18, Section 1001).

Certification Regarding Conflict of Interest

The AOR is required to complete certifications stating that the organization has implemented and is enforcing a written policy on conflicts of interest (COI), consistent with the provisions of AAG Chapter IV.A.; that, to the best of his/her knowledge, all financial disclosures required by the conflict of interest policy were made; and that conflicts of interest, if any, were, or prior to the organization's expenditure of any funds under the award, will be, satisfactorily managed, reduced or eliminated in accordance with the organization's conflict of interest policy. Conflicts that cannot be satisfactorily managed, reduced or eliminated and research that proceeds without the imposition of conditions or restrictions when a conflict of interest exists, must be disclosed to NSF via use of the Notifications and Requests Module in FastLane.

Drug Free Work Place Certification

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent), is providing the Drug Free Work Place Certification contained in Exhibit II-3 of the Grant Proposal Guide.

Debarment and Suspension Certification

(If answer "yes", please provide explanation.)

Is the organization or its principals presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency?

Yes ☐

No ☒

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant is providing the Debarment and Suspension Certification contained in Exhibit II-4 of the Grant Proposal Guide.

Certification Regarding Lobbying

This certification is required for an award of a Federal contract, grant, or cooperative agreement exceeding \$100,000 and for an award of a Federal loan or a commitment providing for the United States to insure or guarantee a loan exceeding \$150,000.

Certification for Contracts, Grants, Loans and Cooperative Agreements

The undersigned certifies, to the best of his or her knowledge and belief, that:

- (1) No Federal appropriated funds have been paid or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.
- (2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, "Disclosure of Lobbying Activities," in accordance with its instructions.
- (3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1352, Title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than \$10,000 and not more than \$100,000 for each such failure.

Certification Regarding Nondiscrimination

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is providing the Certification Regarding Nondiscrimination contained in Exhibit II-6 of the Grant Proposal Guide.

Certification Regarding Flood Hazard Insurance

Two sections of the National Flood Insurance Act of 1968 (42 USC §4012a and §4106) bar Federal agencies from giving financial assistance for acquisition or construction purposes in any area identified by the Federal Emergency Management Agency (FEMA) as having special flood hazards unless the:

- (1) community in which that area is located participates in the national flood insurance program; and
- (2) building (and any related equipment) is covered by adequate flood insurance.

By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) or Individual Applicant located in FEMA-designated special flood hazard areas is certifying that adequate flood insurance has been or will be obtained in the following situations:

- (1) for NSF grants for the construction of a building or facility, regardless of the dollar amount of the grant; and
- (2) for other NSF grants when more than \$25,000 has been budgeted in the proposal for repair, alteration or improvement (construction) of a building or facility.

Certification Regarding Responsible Conduct of Research (RCR)

(This certification is not applicable to proposals for conferences, symposia, and workshops.)

By electronically signing the Certification Pages, the Authorized Organizational Representative is certifying that, in accordance with the NSF Proposal & Award Policies & Procedures Guide, Part II, Award & Administration Guide (AAG) Chapter IV.B., the institution has a plan in place to provide appropriate training and oversight in the responsible and ethical conduct of research to undergraduates, graduate students and postdoctoral researchers who will be supported by NSF to conduct research. The AOR shall require that the language of this certification be included in any award documents for all subawards at all tiers.

CERTIFICATION PAGE - CONTINUED

<p>By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that there is organizational support for the proposal as required by Section 526 of the America COMPETES Reauthorization Act of 2010. This support extends to the portion of the proposal developed to satisfy the Broader Impacts Review Criterion as well as address the broader impacts and intellectual merit activities to be undertaken.</p>			
<p>Certification Regarding Organizational Support</p>			
<p>When the proposal exceeds \$5,000,000, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal tax obligations:</p>			
<p>(1) has filed all Federal tax returns required during the three years preceding this certification;</p>			
<p>(2) has not been convicted of a criminal offense under the Internal Revenue Code of 1986; and</p>			
<p>(3) has not, more than 90 days prior to this certification, been notified of any unpaid Federal tax assessment for which the liability remains unassessed, unless the assessment is the subject of an installment agreement or offer in compromise that has been approved by the Internal Revenue Service and is not in default, or the assessment is the subject of a non-frivolous administrative or judicial proceeding.</p>			
<p>Certification Regarding Unpaid Federal Tax Liability</p>			
<p>When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Federal Tax Liability:</p>			
<p>By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has no unpaid Federal tax liability that has been assessed, for which all judicial and administrative remedies have been exhausted or lapsed, and that is not being paid in a timely manner pursuant to an agreement with the authority responsible for collecting the tax liability.</p>			
<p>Certification Regarding Criminal Convictions</p>			
<p>When the proposing organization is a corporation, the Authorized Organizational Representative (or equivalent) is required to complete the following certification regarding Criminal Convictions:</p>			
<p>By electronically signing the Certification Pages, the Authorized Organizational Representative (or equivalent) is certifying that the corporation has not been convicted of a felony criminal violation under any Federal law within the 24 months preceding the date on which the certification is signed.</p>			
<p>NAME</p>			
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<p>TELEPHONE NUMBER</p>		<p>EMAIL ADDRESS</p>	
<p>FAX NUMBER</p>			

PROJECT SUMMARY

Overview:

Because of their persistence, bioaccumulation potential, and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are being replaced with short-chain PFASs and fluorinated alternatives. Almost no information exists about the occurrence of fluorinated alternatives and their behavior during water treatment. The overall goal of the proposed research is to begin to fill this knowledge gap by studying one class of fluorinated alternatives, perfluoro(poly)ethers (PFPEs). Specific research objectives include to (1) develop a quantitative liquid chromatography-tandem mass spectrometry (LC-MS/MS) method for the analysis of 13 PFPEs in water, (2) apply the LC-MS/MS method to (a) determine PFPE fate between a known PFPE discharge location and the intake of the Sweeney water treatment plant (WTP), which is operated by our industry partner, the Cape Fear Public Utilities Authority (CFPUA), (b) quantify PFPE concentrations and mass flows at the intake of the Sweeney WTP, (3) in collaboration with the CFPUA, trace parcels of water through the Sweeney WTP to quantify PFPE removal/transformation in full-scale water treatment processes, and (4) trace parcels of water through the Wilmington, NC water distribution system to determine PFPE fate during drinking water distribution and use PFPE concentration data to estimate human exposure to PFPEs via consumption of drinking water. The proposed EAGER/GOALIE research is designed to confirm seed data indicating that PFPEs dominate the PFAS signature both in the source and in the finished drinking water of our industry partner. Results are expected to provide the basis for a broader investigation of the behavior of fluorinated alternatives in natural and engineered systems.

Intellectual Merit :

As long-chain PFASs are being phased out, numerous fluorinated alternatives are being brought to market. Very little is known about the identity of fluorinated alternatives, and information about their occurrence in the aquatic environment and their behavior during water treatment is completely absent from the peer-reviewed literature. By beginning to fill at least some of the vast knowledge gaps surrounding fluorinated alternatives, results from the proposed research are expected to be transformative in numerous ways. For example, we will (1) introduce a new large-volume, direct-injection LC-MS/MS method capable of quantifying PFPE concentrations in aqueous samples, (2) develop the first quantitative PFPE occurrence data set for a drinking water source and finished drinking water, and (3) develop data supporting PFPE exposure assessment via drinking water consumption.

Broader Impacts :

Given the data scarcity surrounding fluorinated alternatives, it is anticipated that the results of this research will receive wide interest. For example, the analytical method developed in this research will be useful for characterizing PFPE concentrations in other watersheds impacted by industrial wastewater discharges. The grant will contribute to the education of one PhD student, who will be introduced to advanced analytical methods for the determination of emerging contaminants. Furthermore, the collaboration with the CFPUA will offer the PhD student hands-on experiences with state-of-the-art water treatment technologies at a mid-sized WTP. The PhD student will be a member of a research team that includes members from academia, a public water utility, and EPA scientists. Together, we plan to reach out to a wide range of constituencies to communicate the findings of our research. We anticipate that coordinated efforts between affected utilities, regulatory agencies at the state and federal level, and identified sources will lead to the elimination and/or reduction of PFPE concentrations in the Cape Fear River.

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Project Summary (not to exceed 1 page)

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Project Description (including Results from Prior

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specific program announcement/solicitation or if approved in
advance by the appropriate NSF Assistant Director or designee)

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Biographical Sketches (Not to exceed 2 pages each)

Budget
(Plus up to 3 pages of budget justification)

Current and Pending Support

Facilities, Equipment and Other Resources

Special Information/Supplementary Documents
(Data Management Plan, Mentoring Plan
and Other Supplementary Documents)

Appendix (List below.)

(Include only if allowed by a specific program announcement/
solicitation or if approved in advance by the appropriate NSF
Assistant Director or designee)

Appendix Items:

*Proposers may select any numbering mechanism for the proposal. The entire proposal however, must be paginated.
Complete both columns only if the proposal is numbered consecutively.

Project Description

1. GOALI Project Proposal Form (Snapshot)

Project Title: Perfluoro(poly)ethers – a new class of drinking water contaminants

University Participant: North Carolina State University, Raleigh, NC

Industry Participant: Cape Fear Public Utilities Authority (CFPUA), Wilmington, NC

Project head (PI): Detlef Knappe, Professor

Total NSF Request: \$89,849

Project Description: Because of ecotoxicological and human health concerns, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are being replaced with short-chain PFASs and fluorinated alternatives. Almost no information exists about the occurrence of fluorinated alternatives and their behavior during water treatment. The overall goal of the proposed research is to begin to fill this knowledge gap by studying one class of fluorinated alternatives, perfluoro(poly)ethers (PFPEs).

Experimental plan: The experimental plan is designed to meet the four research objectives described in detail in the following project description. During the first four months, we plan to develop a liquid chromatography-tandem mass spectrometry (LC-MS/MS) method to quantify aqueous PFPE concentrations. During the following 4 months, we will apply the LC-MS/MS method in conjunction with stream sampling campaigns to (1) quantify PFPE occurrence and (2) assess PFPE fate in the Cape Fear River between a known PFPE source and CFPUA's intake location. Finally, we will collaborate closely with the CFPUA to conduct sampling campaigns designed to determine (1) PFPE removal/transformation in individual unit operations of CFPUA's water treatment plant, and (2) PFPE fate during drinking water distribution.

Related work elsewhere: None

Is this project unique or if it is based on previous research, how does it differ? The proposed project is unique.

Milestones: (1) Development of LC-MS/MS method to quantify PFPE concentrations, (2) completion of stream sampling campaigns and associated PFPE analyses with an assessment of PFPE persistence, (3) completion of sampling campaigns to characterize PFPE removal/transformation in full-scale water treatment processes, and (4) determination of PFPE concentrations and variability in finished drinking water and associated exposure assessment.

Deliverables: (1) Analytical method to quantify PFPEs, (2) assessment of PFPE persistence in natural and engineered systems, and (3) estimate of PFPE exposure via drinking water consumption.

How the project may be transformative and/or benefit society: Very little is known about the identity of fluorinated alternatives, and information about their occurrence in the aquatic environment and their behavior during water treatment is completely absent from the peer-reviewed literature. Results from the proposed research will fill some of these vast knowledge gaps. The project is expected to be transformative because we anticipate that current analytical methods for PFAS determination miss the majority of PFASs present in water sources impacted by industrial wastewater discharges. Results from the proposed research are expected to provide the basis for outreach efforts, co-organized by NCSU and CFPUA, designed to minimize PFPE concentrations in the drinking water of affected communities.

Potential Commercialization: N/A

Estimated Start Date: 08/15/2015

Estimated Completion Date: 08/14/2016

2. Introduction, Background, and Motivation

Perfluoroalkyl substances (PFASs) are aliphatic organic compounds in which all C-H bonds of a non-fluorinated analogue have been replaced by C-F bonds (Buck et al. 2011). PFASs serve as processing aids in the production of fluoropolymers such as polytetrafluoroethylene (PTFE, aka Teflon) or polyvinylidene fluoride (PVDF) and are active ingredients in stain repellents (e.g. Scotchgard), firefighting foams, and food-contact paper coatings. Until about 2000, use of long-chain PFAS chemistries, defined as perfluorocarboxylic acids (PFCAs) with 8 or more carbon atoms and perfluorosulfonic acids (PFSAs) with 6 or more carbon atoms (Buck et al. 2011, OECD 2011), was dominant. The most well-studied examples of long-chain PFASs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Increasing evidence about ecotoxicological and human health effects associated with exposure to long-chain PFASs has led to efforts to eliminate their production and use. As long-chain PFAS chemistries are being abandoned, industry is moving towards (1) short-chain PFAS chemistries and (2) fluorinated alternatives (Wang et al. 2013, 2015; Scheringer et al. 2014). The move towards fluorinated alternatives represents a complex challenge from a standpoint of environmental and human health assessment. As noted in the Helsinger Statement, little information is available about production volumes, uses, properties, and biological effects of fluorinated alternatives (Scheringer et al. 2014).

One class of fluorinated alternatives are perfluoro(poly)ethers (PFPEs), which were recently identified in Cape Fear River water and in finished drinking water of the Sweeney water treatment plant (WTP), which is operated by our industry partner, the Cape Fear Public Utilities Authority (CFPUA). The identified PFPEs are perfluorocarboxylic acids containing one or more ether bonds, and formulas for the PFPEs are summarized in Table 1.

Table 1. PFPEs identified in a Cape Fear River water sample collected on August 27, 2014

Name	CAS #	Formula	Molecular Weight
Perfluoro(2-oxapropanoic) acid	674-13-5	C ₃ HF ₅ O ₃	180.0
Perfluoro(3-oxabutanonic) acid	377-73-1	C ₄ HF ₆ O ₃	230.0
Perfluoro(4-oxapentanoic) acid	863090-89-5	C ₅ HF ₇ O ₃	280.0
Perfluoro(2-methyl-3-oxahexanoic) acid ("GenX")	13252-13-6	C ₆ HF ₁₁ O ₃	330.1
Carboxylic acids with one ether group (C _n HF _{2n-1} O ₃)			
Perfluoro(3,5-dioxahexanoic) acid	39492-88-1	C ₆ HF ₉ O ₄	246.0
Carboxylic acid with two ether groups (C _n HF _{2n-1} O ₄)			
Perfluoro(3,5,7-trioxaoctanoic) acid	39492-89-2	C ₇ HF ₉ O ₅	312.0
Carboxylic acid with three ether groups (C _n HF _{2n-1} O ₅)			
Perfluoro(3,5,7,9-tetraoxadecanoic) acid	39492-90-5	C ₈ HF ₁₁ O ₆	378.1

The structure of one of the identified PFPEs, known as GenX, was introduced in a paper by Wang et al. (2013), but to the knowledge of the PI and his collaborators, no peer-reviewed publications and only one conference paper (Strynar et al. 2012) document GenX occurrence in the environment. Furthermore, no published information is available about the other PFPEs identified in the Cape Fear River water and drinking water samples. Peak areas for some of the new PFPEs were 1-2 orders of magnitude larger than those associated with GenX, which was present at a concentration of ~450 ng/L. The seed data for the proposed research suggest that fluorinated alternatives are beginning to dominate the PFAS signature of wastewater-impacted

surface waters and illustrate the need to (1) identify and quantify the presence of fluorinated alternatives in the aquatic environment and (2) develop information about the behavior of fluorinated alternatives in the aquatic environment and in engineered water treatment systems.

3. Hypotheses and Objectives

Hypothesis 1: Recently discovered perfluoro(poly)ethers (PFPEs) are persistent organic pollutants that dominate the PFAS signature downstream of fluorochemical production facilities. This hypothesis is supported by recently collected accurate mass liquid chromatography-time-of-flight-mass spectrometry (LC-TOF/MS) data that led to the discovery of previously unidentified PFPEs in Cape Fear River water (Strynar et al. 2014) and LC tandem mass spectrometry (LC-MS/MS) data showing that area counts for PFPEs greatly exceed those of more commonly targeted perfluoroalkylcarboxylic acids (PFCAs) and perfluoroalkylsulfonic acids (PFSAAs). To test hypothesis 1, we propose to conduct the activities shown under objectives 1 and 2.

- **Objective 1:** Develop a quantitative LC-MS/MS method for the analysis of 13 PFPEs.
- **Objective 2:** Apply the LC-MS/MS method to (a) determine PFPE fate between a known PFPE discharge location and the intake of the Sweeney WTP (~90 river kilometers), (b) quantify PFPE concentrations and mass flows at the intake of the Sweeney WTP. To our knowledge, these data will quantitatively document for the first time the occurrence of PFPEs in a US drinking water source.

Hypothesis 2: Incumbent water treatment technologies do not effectively remove/transform PFPEs. This hypothesis is supported by preliminary LC-MS/MS data showing little change in PFPE area counts (and concentrations for one PFPE, GenX) during raw and settled water ozonation, biofiltration, UV and chlorine disinfection in the Sweeney WTP. A corollary of this hypothesis is that drinking water is an important PFPE exposure pathway. To test hypothesis 2 and its corollary, we propose to conduct the activities shown under objectives 3 and 4.

- **Objective 3:** In collaboration with the CFPWA, trace parcels of water through the Sweeney WTP to quantify PFPE removal/transformation in full-scale water treatment processes.
- **Objective 4:** Working with CFPWA, trace parcels of water through the Wilmington, NC water distribution system to determine PFPE fate during drinking water distribution. Use PFPE concentration data to estimate human exposure to PFPEs via consumption of drinking water.

4. Technical Approach

Objective 1. Develop a quantitative LC-MS/MS method for the analysis of PFPEs.

Approach: The basis for this activity is an existing large-volume direct injection LC-MS/MS method (Dudley et al. 2015) we are currently using to determine the concentrations of 7 PFCAs (first 7 compounds in Table 2) as well as the PFSAAs perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), and PFOS. An Agilent 1100 Series LC system equipped with a 4.6 mm x 50 mm HPLC column (FluoroFlash, Fluorous Technologies Inc. or Kinetex C18 5 µm 100Å, Phenomenex Inc.) is used for PFAS separation. The LC is connected to a PE Sciex API 3000 triple quadrupole MS that is operated in the negative electrospray ionization (ESI)

mode using multiple reaction monitoring (MRM). Ionization and collision cell parameters were optimized for each individual analyte.

Table 2. Proposed List of Target Compounds

Name	CAS #	Formula	Molecular Weight
Carboxylic acids without an ether group ($C_nH_{2n-1}O_2$)			
Perfluorobutanoic acid	375-22-4	$C_4HF_7O_2$	214.0
Perfluoropentanoic acid*	2706-90-3	$C_5HF_9O_2$	264.0
Perfluorohexanoic acid*	307-24-4	$C_6HF_{11}O_2$	314.1
Perfluorohexanoic acid*	375-85-9	$C_7HF_{13}O_2$	364.1
Perfluorooctanoic acid*	335-67-1	$C_8HF_{15}O_2$	414.1
Perfluorononanoic acid	375-95-1	$C_9HF_{17}O_2$	464.1
Perfluorodecanoic acid	335-76-2	$C_{10}HF_{19}O_2$	514.1
Carboxylic acids with one ether group ($C_nH_{2n-1}O_3$)			
Perfluoro(2-oxapropanoic) acid*	674-13-5	$C_3HF_5O_3$	180.0
Perfluoro(3-oxabutanoic) acid*	377-73-1	$C_4HF_7O_3$	230.0
Perfluoro(4-oxapentanoic) acid*	863090-89-5	$C_5HF_9O_3$	280.0
Perfluoro(2-methyl-3-oxahexanoic) acid ("GenX")*	13252-13-6	$C_6HF_{11}O_3$	330.1
Perfluoro(5-oxa-6-dimethylhexanoic) acid	801212-59-9	$C_7HF_{13}O_3$	380.1
Perfluoro(2-methyl-3-oxaoctanoic) acid	N/A	$C_8HF_{15}O_3$	430.1
Perfluoro(8-oxa-9-dimethylnonanoic) acid	32347-41-4	$C_{10}HF_{19}O_3$	530.1
Carboxylic acids with two ether groups ($C_nH_{2n-1}O_4$)			
Perfluoro(3,5-dioxahexanoic) acid*	39492-88-1	$C_4HF_7O_4$	246.0
Perfluoro(3,6-dioxadecanoic) acid	137780-69-9	$C_8HF_{15}O_4$	446.1
Carboxylic acids with three ether groups ($C_nH_{2n-1}O_5$)			
Perfluoro(3,5,7-trioxaoctanoic) acid*	39492-89-2	$C_5HF_9O_5$	312.0
Perfluoro(3,6,9-trioxadecanoic) acid	151772-59-7	$C_7HF_{13}O_5$	412.1
Perfluoro(3,6,9-trioxatridecanoic) acid	330562-41-9	$C_{10}HF_{19}O_5$	562.1
Carboxylic acid with four ether groups ($C_nH_{2n-1}O_6$)			
Perfluoro(3,5,7,9-tetraoxadecanoic) acid*	39492-90-5	$C_6HF_{11}O_6$	378.1

*Identified in Cape Fear River water sample collected on August 27, 2014

Using an authentic standard, we recently added GenX to the list of analytes of our LC-MS/MS method. Authentic standards are commercially available for most of the ether compounds shown in Table 2 and will be used to optimize ionization and collision cell parameters. Custom synthesis of one or two of the compounds shown in Table 2 may be necessary. For PFPE quantitation, the use of custom-made mass-labeled PFPEs as internal standards will be explored, but will likely be cost-prohibitive. Two alternative quantitation approaches will be explored: (1) reference analyte area counts to area counts of commercially available mass-labeled PFCEs with (closely) matched numbers of perfluorinated carbon atoms (e.g. Dudley et al. 2015) and (2) for Cape Fear River and Sweeney WTP samples, use PFPEs that do not occur in Cape Fear River water as internal standards. Limits of quantitation (LOQs) for current analytes are in the range of 10-25 ng/L. LOQs for new analytes will be determined as described by Lindstrom et al. (2009).

Objective 2: Apply LC-MS/MS method to (a) determine PFPE fate between a known PFPE discharge location and the intake of the Sweeney WTP (~90 river kilometers), (b) quantify PFPE concentrations and mass flows at the intake of the Sweeney WTP,

Approach: To determine PFPE fate in the Cape Fear River, samples will be taken at five locations located approximately 0.5, 11, 37, 76, and 90 km downstream of the PFPE source. In addition, one background sample will be collected upstream of the PFPE discharge location. Sampling points include three lock and dam locations, a site upstream of a cable ferry dock, and a river access road below a bridge (heavy traffic on narrow bridge precludes safe sampling from the bridge). Samples will be collected with a pole sampler that holds 1-L HDPE bottles. Similar to Fono et al. (2006), sample collection will be conducted over a period of four days, proceeding in downstream and upstream directions on alternate days. Two sampling campaigns will be conducted over a 4-month period to capture different hydrological conditions. Stream gauges operated by the US Geological Survey record flow, river stage and precipitation every 15 minutes at the location closest to the PFPE discharge and at the Sweeney WTP intake. Flow at other sampling stations will be estimated from USGS gauge data and drainage area values.

Expected data and data interpretation: Data generated under this objective will permit a quantitative answer to the questions:

1. What are PFPE concentrations and mass flows in the Cape Fear River?
2. Do PFPEs behave conservatively?

Results from the targeted LC-MS/MS analyses will provide concentration data for the 20 PFASs shown in Table 2 as well as for three perfluoroalkyl sulfonic acids (PFBS, PFHxS, PFOS). In addition to concentration data, PFAS mass flows will be calculated. Mass flows will give an indication of the variability in PFAS releases at the source. It should be noted that mean streamflow values along the 90-km stretch of river remain relatively constant in the absence of local storms (USGS 2014), making the study location ideal for assessing potential PFPE losses in the river as a result of natural transformation processes such as photolysis and biodegradation.

Objective 3: In collaboration with the CFPUA, trace parcels of water through the Sweeney WTP to quantify PFPE removal/transformation in full-scale water treatment processes.

Approach: To determine whether PFPE removal/transformation takes place during full-scale drinking water treatment, the PhD student supported by this grant will closely work with our industry partner, the CFPUA, to track parcels of water through the Sweeney WTP in Wilmington, NC. During the course of the research, the PhD student will be a resident at CFPUA to become familiar with the design and operation of the Sweeney WTP and to develop information about residence time distributions of individual unit processes. This information will be used to develop a sampling plan that permits tracking of water parcels through the WTP.

The Sweeney WTP employs a range of conventional and advanced water treatment processes, including raw and settled water ozonation, granular activated carbon (GAC) biofiltration, and UV disinfection. Samples will be taken at the following locations:

- (1) Raw water intake, (2) Effluent of pre-ozone reactor, (3) Effluent of settling basin, (4) Effluent of settled water ozone reactor, (5) Effluent of GAC biofilter, (6) Effluent of UV reactor, and (7) Point-of-entry (POE) to distribution system (following contact with free chlorine)

The new quantitative LC-MS/MS method will be applied to quantify PFPE fate in individual treatment processes. Based on screening data collected for GenX (concentration data, Fig. 2) and new PFPEs (peak areas), we hypothesize that none of the treatment processes in the Sweeney WTP are capable of removing/transforming PFPEs. In other words, PFPEs are likely persistent

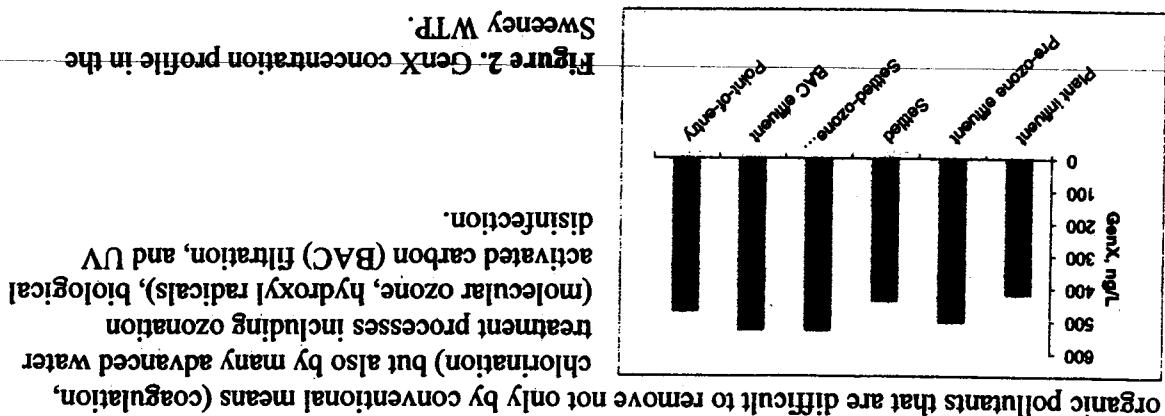


Figure 2. GenX concentration profile in the Sweeney WTP.

organic pollutants that are difficult to remove not only by conventional means (coagulation, chlorination) but also by many advanced water treatment processes including ozonation (molecular ozone, hydroxyl radicals), biological activated carbon (BAC) filtration, and UV disinfection.

Objective 4: Working with CFPWA, trace parcels of water through the Wilmington, NC water distribution system to determine PFPE fate during drinking water distribution. Use PFPE concentration data to estimate human exposure to PFPEs via consumption of drinking water. **Approach:** To establish whether or not PFPEs behave conservatively during distribution, two approaches will be followed:

1. Bench-scale aging experiments will be conducted by collecting finished water samples containing free chlorine in HDPE or brown glass bottles (bottle selection based on screening experiments) and stored in the dark for up to 10 days ($T = 20^{\circ}\text{C}$). Samples will be analyzed by LC-MS/MS after different storage times to determine whether PFPE concentrations change.

2. Using an existing calibrated distribution system model, water ages at distribution system sampling points will be estimated. Using these water age estimates, parcels of water leaving the Sweeney WTP will be tracked by collecting a finished water sample at time zero and distribution system samples at their respective water age estimates. Data from these samples will inform the research team whether factors such as biofilms and/or interactions with pipe walls affect PFPE fate in the distribution system.

Exposure estimates will be made from finished water PFPE concentrations unless PFPE concentrations change substantially in the distribution system. To estimate variability in PFPE concentrations, CFPWA staff will collect daily samples and composite these samples over a period of one week. Weekly composite samples will be analyzed over a period of 2 months to establish PFPE concentration ranges in the finished water of the Sweeney WTP. Exposure calculations will be based on EPA's Life-Stage Classification for Exposure Assessment (e.g. Hines et al. 2010, USEPA 2005, 2006b).

5. Intellectual Merit

As long-chain PFASs are being phased out, numerous fluorinated alternatives are being brought to market. Very little is known about the identity of fluorinated alternatives, and information about their occurrence in the aquatic environment and their behavior during water treatment is completely absent from the peer-reviewed literature. By beginning to fill at least some of the vast knowledge gaps surrounding fluorinated alternatives, results from the proposed research are expected to be transformative in numerous ways. For example, we will (1) introduce a new large-volume, direct-injection LC-MS/MS method capable of quantifying PFPE concentrations

in aqueous samples, (2) develop the first quantitative PFPE occurrence data set for a drinking water source and finished drinking water, and (3) develop data supporting PFPE exposure assessment via drinking water consumption.

6. Broader Impacts

This grant will contribute to the education of one female US PhD student, who will be joining my research group in August 2015. The PhD student will be introduced to advanced analytical methods for the determination of emerging contaminants. Furthermore, the collaboration with the CFPUA will offer the PhD student hands-on experiences with state-of-the-art water treatment technologies at a mid-sized WTP. The PhD student will be a member of a research team that includes members from academia, a public water utility, and EPA scientists. Together, we plan to reach out to a wide range of constituencies to communicate the findings of our research. We anticipate that coordinated efforts between affected utilities, regulatory agencies at the state and federal level, and identified sources will lead to the elimination and/or reduction of PFPE concentrations in the Cape Fear River. Furthermore, the analytical method developed in this research will support the determination of PFPE concentrations in other watersheds impacted by industrial wastewater discharges.

7. Schedule and Project Management

During the first two weeks of the project, a one-day coordination meeting will be held to introduce all research team members, review the research and data management plans, and to assign tasks. Subsequently, project team meetings will be held quarterly with meeting locations alternating between NCSU and CFPUA. During summer 2016, the NCSU PhD student will reside at CFPUA to become familiar with full-scale unit treatment processes and the Wilmington water distribution system. The PhD student will also collaborate closely with CFPUA staff on sampling campaigns proposed under objectives 3 and 4 (Table 3). As shown in Table 3, the project team expects to complete the proposed research within 12 months of the project start date. Two industrial seminars will be held to summarize research results and their implications on drinking water quality and treatment. One of the seminars will be held at CFPUA, and personnel from other utilities that are likely impacted by PFASs/PFPEs will be invited. The second seminar will be held at the offices of the North Carolina Department of Environment and Natural Resources (DENR). Representatives from utilities, engineering firms, DENR, and other water quality and treatment professionals will be invited. A final report will be submitted to NSF as shown in Table 3, and at least one manuscript will be submitted for peer-review at the same time.

Table 3. Schedule for proposed research, coordination, and reporting activities

Objective	Month	1	2	3	4	5	6	7	8	9	10	11	12
Method development (Objective 1)													
Stream sampling (Objective 2)													
Sweeney WTP samples (Objective 3)													
Distribution system samples and exposure assessment (Objective 4)													
Industrial seminars													
Manuscript and NSF Final Report													

8. Results from prior NSF support

NSF award number: #1449768. **Amount of support:** \$50,000. **Period of support:** 8/15/14 – 7/31/15. **Title:** RAPID; GOAL: Sources of 1,4-Dioxane in the Cape Fear River Watershed of North Carolina and Treatment Options for 1,4-Dioxane Control.

Summary of results:

Intellectual Merit: A new analytical method for the analysis of 1,4-dioxane was developed. A heated purge-and-trap preconcentration step was coupled with ion-trap gas chromatography-mass spectrometry (GC/MS) operated in selected-ion storage mode. 1,4-dioxane concentrations are quantified relative to mass-labeled 1,4-dioxane internal standard. The new analytical method is sensitive (limit of quantitation: 0.15 µg/L), fully automated, accurate in a wide range of background water matrices, and is currently supporting the analysis of large numbers of samples being generated by stream sampling campaigns, daily composite sampling at WTPs, and bench-scale experiments designed to develop treatment options. In coordination with our industry partner, the Fayetteville Public Works Commission, and the North Carolina Department of Natural Resources (DENR), we designed a stream sampling plan to identify 1,4-dioxane sources. Our results have identified three North Carolina communities as key sources of 1,4-dioxane and pretreatment managers in these communities are now conducting sewer trunk line studies to identify sources of the contamination within the sewer collection system. Experiments are underway to identify/develop effective point-of-use treatment options for 1,4-dioxane removal from tap water.

Broader impacts: The Cape Fear River and its headwaters are the source of drinking water for about 400,000 North Carolinians. Because important 1,4-dioxane sources are located in the headwaters, elevated levels of 1,4-dioxane are found in the drinking water of most municipalities in the watershed as well as in the potable water of some purchase systems located in neighboring watersheds. Coordinated activities between NCSU, public utilities, and DENR are expected to generate data that will provide the basis for managing 1,4-dioxane sources in the Cape Fear River watershed. Furthermore, the analytical method that was developed with this grant is expected to facilitate future data collection for 1,4-dioxane, a contaminant that occurs in ~12% of US drinking water samples (USEPA 2015). The grant supports the training of a female PhD student of Hispanic origin.

Publication resulting from award: An ES&T manuscript draft describing the new analytical method and its application is close to submission. A presentation was given at the 2014 Water Quality Technology Conference (New Orleans, Nov. 16-19, 2014) that provided an overview of the new analytical method and its application. Results from this research were also presented at a NSF workshop (Fostering advances in water resource protection and crisis communication, lessons learned from recent disasters, Sheperdstown, WV, May 27-29, 2015). Finally, our 1,4-dioxane research was featured in an NSF Science Nation video that was released on May 4, 2015.

REFERENCES

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- Dudley, L.A., E.C. Arevalo, and D.R.U. Knappe. 2015. *Removal of perfluoroalkyl substances by powdered activated carbon adsorption and anion exchange*. Water Research Foundation: Denver, CO.
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- Strynar, M., R. McMahan, S. Liang, S. Dagnino, A. Lindstrom, et al. 2014. Use of accurate mass LC/TOF for the identification of unknown polyfluorinated contaminants in water. Agilent Environmental Techniques Workshop, Tucson, AZ, March 18-19.
- Strynar, M., S. Dagnino, A. Lindstrom, E. Andersen et al. 2012. Identification of novel polyfluorinated compounds in natural waters using accurate mass TOFMS. SETAC N. America Meeting, Nov. 10-15, Long Beach, CA.
- USEPA. 2015. Occurrence Data: Accessing Unregulated Contaminant Monitoring Data. Available from: <http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/data.cfm> (accessed June 10, 2015).
- USEPA. 2006. A framework for assessing health risks of environmental exposures to children. EPA/600/R-05/093F. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC.
- USEPA. 2005. Guidance on selecting age groups for monitoring and assessing childhood exposures to environmental contaminants. EPA/630/P-03/003F. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC.
- USGS. 2014. Water Watch. Available from: http://waterwatch.usgs.gov/index.php?r=nc&id=ww_current (accessed Oct. 30, 2014).
- Wang, Z., I.T. Cousins, M. Scheringer, and K. Hungerbühler. 2015. Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status quo, ongoing challenges and possible solutions. *Environment International* 75: 172-179.
- Wang, Z., I.T. Cousins, M. Scheringer, and K. Hungerbühler. 2013. Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and their potential precursors. *Environment International* 60: 242-248.

Delft R.U. Knappe Department of Civil, Construction, and Environmental Engineering, North Carolina State University

Professional Preparation

University of Illinois, Urbana, IL	Civil Engineering	B.S., May 1989
University of Illinois, Urbana, IL	Environmental Engineering	M.S., May 1991
University of Illinois, Urbana, IL	Environmental Engineering	Ph.D., January 1996

Appointments

2008 – present	Professor, Department of Civil, Construction, and Environmental Engineering, NC State University, Raleigh, NC
2013 (1/1-6/30)	Visiting Scholar, US EPA, Research Triangle Park, NC
2002 – 2008	Associate Professor, Department of Civil, Construction, and Environmental Engineering, NC State University, Raleigh, NC
2005 (7/1-12/31)	Visiting Scholar, EAWAG, Swiss Federal Institute of Technology (ETH), Zurich, Switzerland
1996 - 2002	Assistant Professor, Dept. of Civil Engineering, NC State University, Raleigh, NC

Publications most closely related to the proposed project

- Dudley, L.A., E.C. Arévalo, and D.R.U. Knappe. *Removal of perfluoralkyl substances by powdered activated carbon adsorption and anion exchange*. Water Research Foundation: Denver, CO, 2015.
- Kennedy, A.M.; A.M. Reimert; D.R.U. Knappe; I. Ferrer; and R.S. Summers. "Full- and pilot-scale GAC adsorption of organic micropollutants." *Water Res.*, 68: 238-248, 2015.
- Kearns, J.P.; D.R.U. Knappe; and R.S. Summers. "Synthetic organic water contaminants in developing communities: An overlooked challenge addressed by adsorption with locally generated char." *J. WASH Dev.*, 4(3): 422-436, 2014.
- Rossner, A.; S.A. Snyder; and D.R.U. Knappe. "Removal of an emerging contaminant mixture by alternative adsorbents." *Water Res.*, 43(15): 3787-3796, 2009.
- Li, L.; P.A. Quinlivan; and D.R.U. Knappe. "Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution." *Carbon*, 40(12): 2085-2100, 2002.

Other significant publications

- Kovalova, L.; D.R.U. Knappe; K. Lehnberg; K. Kazner; and J. Hollender. "Removal of highly polar micropollutants from wastewater by powdered activated carbon." *Environ. Sci. Poll. Res.*, 20(6): 3607-3615, 2013.
- Baeza, A.C. and D.R.U. Knappe. "Transformation kinetics of biochemically active compounds in low-pressure UV photolysis and UV/H₂O₂ advanced oxidation processes." *Water Res.*, 45(15): 4531-4543, 2011.
- Velten, S.; D.R.U. Knappe; J. Traber; H.P. Kaiser; U. von Gunten; M. Bolter; and S. Meylan. "Characterization of natural organic matter adsorption in granular activated carbon adsorbents." *Water Res.*, 45(13): 3951-3959, 2011.
- Teuten, E.L.; J.M. Saquing; D.R.U. Knappe; M.A. Barlaz; S. Jonsson; A. Björn; S.J. Rowland; R.C. Thompson; T.S. Galloway; R. Yamashita; D. Ochi; Y. Watanuki; M.P. Zakaria; Y. Ogata; H. Hirai; S. Iwasa; K. Mizukawa; Y. Hagino; A. Imamura; M. Saha; and H. Takada. "Transport and release of chemicals from plastics to the environment and to wildlife." *Philosophical Transactions of The Royal Society B*, 364: 2027-2045, 2009.
- Li, L.; P.A. Quinlivan; and D.R.U. Knappe. "Predicting Adsorption Isotherms for Aqueous Organic Micropollutants from Activated Carbon and Pollutant Properties." *Environ. Sci. Tech.*, 39(9): 3393-3400, 2005.

Synergistic Activities:

- Meeting/Symposium/Committee Leadership:
 - Organizer for special topic session "Water Treatment with Superfine Powdered Activated Carbon for Organics Removal," AWWA Water Quality Technology Conference, 2015
 - Organizer for special topic session "Activated Carbon Adsorption," AWWA Annual Conf., 2013
 - Co-organizer of ACS Symposium "Advances in Adsorption Processes," Spring 2008.
 - AWWA Activated Carbon Standards Committee Member, 2003-present
 - AWWA Organic Contaminants Research Committee Member, 2000-2005, 2007-present
 - Technical and research advisor for the NCSU Student Chapter of Engineers Without Borders, Fall 2006-present.
- Representative Scholarly and Professional Honors
 - Thesis advisor for the 1st place winner in the American Water Works Association Academic Achievement Award competition for best Master's Thesis, 2013
 - Outstanding Teacher, NC State University, 2011
 - Thesis advisor for the 2nd place winner in the American Water Works Association Academic Achievement Award competition for best Master's Thesis, 2007
 - AWWA Water Science & Research Division Best Poster Award, 2006
 - Bill Horn Kimley-Horn Faculty Award, NC State University, 2003
 - AWWA Water Science & Research Division Best Paper Award, 2001

Collaborators and Co-Editors:

Morton A. Barlaz, NCSU

Joel J. Ducoste, NCSU

Francis L. de los Reyes, NCSU

Howard Weinberg, UNC-Chapel Hill

Mark A. Nanny, University of Oklahoma

Rich McLaughlin, NCSU

Karl Linden, University of Colorado-Boulder

R. Scott Summers, University of Colorado-Boulder

Andrew Lindstrom & Mark Strynar, US EPA, RTP, NC

Thomas Speth, US EPA, Cincinnati, OH

Graduate Advisors and Postdoctoral Sponsors:

Vernon L. Snoeyink (University of Illinois, MS and PhD)

Thesis Advisor & Postgraduate-Scholar Sponsor:

(45 total, 26 MS, 13 PhD, 6 post-graduate scholars)

MS: Andrew Rike, 1998, Harbor Environmental, AR; David Briley, 1999, Hazen & Sawyer, NC; Robert Belk, 1999 Hazen & Sawyer, NC; Neerja Rastogi, 1999, CDM-Smith, NC; Caleb Taylor, 2000; Steven Gandy, 2000, Municipal Engineering Services Company, PA; Patricia Quinlivan (now Chandley), 2001, AECOM, NC; Travis Wagner, 2003, Pure Technologies, MD; Alfred Rossner, 2004, continued for PhD; Lisa Mitchell, 2005, Hydrostructures, NC; Isabella Mezzari, 2006, Shell, TX; Venkata Mandapaka, 2008, CalTrans; Anjali Viswakumar, 2010, EcoServices, Chennai; Qianru Deng, 2010, MWH, WA; Angela Mastropole (now Walsh), 2010, Novozymes, NC; Susan Dunn (now Auten), 2011, Black & Veatch, NY; Leigh-Ann Dudley, 2012, Dewberry, NC; Meredith Fotta (now Miller), 2012, CDM-Smith, NC; Allison Reinert, 2013, Hazen & Sawyer, NC; Elisa Arevalo, 2014, Hazen & Sawyer, NC; Rachel Ingham, 2014, City of Durham, NC; Amber Greune, 2014, Geosyntec, NC; Viking Edeback, 2014, Arcadis, AZ. *Current:* Obatayo Hounwanou, Clark Maness.

PhD: B. Wu, PhD 2002, Rho Inc., NC; L. Li, PhD 2002, California Department of Public Health, CA; Y. Chen, PhD 2003, Novozymes, NC; C. Chun, PhD 2007, VDOT, VA; A.C. Baeza, PhD 2008, Universidad de Concepcion, Chile; A.A. Rossner, PhD 2008, Universidad de Concepcion, Chile; J.M. Saquing, PhD 2009, U. Delaware; B. Yuncu, PhD 2010, Solutions IES, NC. *Current:* Josh Kearns (Scott Summers, chair), Catalina Lopez, Jonathan Moreno, Zachary Hopkins, Amie McElroy.

Postgraduate Scholars: Shannon Bartelt-Hunt, U. Nebraska; Qingdong Qing, Southeast University (China); Erik Rosenfeldt, Hazen & Sawyer, VA; Koichi Ohno, National Institute of Public Health (Japan); Zhang Hua, Tongji University (China). *Current:* Mei Sun.

Michael Ennis Richardson
 Cape Fear Public Utility Authority
 Wilmington, NC

Professional Preparation

Fayetteville Technical Institute, Fayetteville, NC Environmental Engineering Technology A.S., 1975

Appointments

2008 – present	Water Resources Manager, Cape Fear Public Utility Authority, Wilmington, NC
1994 – 2008	Water Treatment Superintendent, City of Wilmington, Wilmington, NC
1991 – 1994	Manager, Cleveland County Sanitary District, Lenoir, NC
1981 – 1991	Superintendent, Montgomery County Water System, Troy, NC
1980 – 1981	Technical Specialist, NC Rural Water Association, Welcome, NC
1978 – 1980	Chief Operator, NE Metropolitan Water, Lenoir, NC
1976 – 1978	Asst Public Works Director, Town of Lenoir, NC

Representative Conference Presentations

Richardson, M.E. and T. 2013. CFPWA: Water resources for the future. NCAWWA Spring Conference, Wilmington, NC.

Richardson, M.E., Johnson, N. and Derr, A. 2013. Meeting the challenges of upgrading the plant control system yields major operations benefits. NCAWWA Annual Conference, Concord, NC.

Richardson, M.E. 2012. Drinking Water Sources – Taste & Odor Plus?? North Carolina Forum on Nutrient Over-Enrichment, Durham, NC.

Coggins, J. and Richardson, M. 2010. Phased approach to constructing the expansion of the Sweeney WTP. NCAWWA Spring Conference, Wilmington, NC.

Synergistic Activities

- NCWaterWARN, Chairman 2008 – present. N.C. Water WARN is a network of water utilities helping each other respond to and recover from emergencies. This organization of water systems works independently of state government to assist members during an emergency. The mission of WARN is to provide expedited access to specialized resources needed to respond to and recover from natural and human caused events that disrupt public and private drinking water and wastewater utilities.
- Board member and committee member NCAWWA, 1981 – present; President 1994 – 95; Vice-Chairman 1992 – 94
- AWWA George Warren Fuller Award, 2010
- Instructor for various schools for NCAWWA, NCAWWA-WEA for over 20 years
- Board of Trustees NCAWWA-WEA 1998 – 2005; Chairman 2004-05; Vice-Chair 2003 – 04;
- Board member of NC Rural Water Association, 1985 – 1991; President 1987 – 88

SUMMARY PROPOSAL BUDGET

YEAR 1

ORGANIZATION North Carolina State University				FOR NSF USE ONLY			
				PROPOSAL NO.		DURATION (months)	
PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR Detlef Knappe				Proposed		Granted	
				AWARD NO.			
A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)				NSF Funded Person-months		Funds Requested By proposer	
				CAL	ACAD	SUMR	Funds granted by NSF (if different)
1. Detlef Knappe - PI				0.00	0.00	0.20	2,500
2.							
3.							
4.							
5.							
6. (0) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)				0.00	0.00	0.00	0
7. (1) TOTAL SENIOR PERSONNEL (1 - 6)				0.00	0.00	0.20	2,500
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)							
1. (0) POST DOCTORAL SCHOLARS				0.00	0.00	0.00	0
2. (0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)				0.00	0.00	0.00	0
3. (1) GRADUATE STUDENTS							0
4. (1) UNDERGRADUATE STUDENTS							24,600
5. (0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)							1,000
6. (0) OTHER							0
TOTAL SALARIES AND WAGES (A + B)							0
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)							28,100
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)							4,525
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.)							32,625
TOTAL EQUIPMENT							
E. TRAVEL							0
1. DOMESTIC (INCL. U.S. POSSESSIONS)							3,000
2. FOREIGN							0
F. PARTICIPANT SUPPORT COSTS							
1. STIPENDS \$ _____				0			
2. TRAVEL _____				0			
3. SUBSISTENCE _____				0			
4. OTHER _____				0			
TOTAL NUMBER OF PARTICIPANTS (0)							
TOTAL PARTICIPANT COSTS							0
G. OTHER DIRECT COSTS							
1. MATERIALS AND SUPPLIES							
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION							10,000
3. CONSULTANT SERVICES							0
4. COMPUTER SERVICES							0
5. SUBAWARDS							0
6. OTHER							0
TOTAL OTHER DIRECT COSTS							17,514
H. TOTAL DIRECT COSTS (A THROUGH G)							27,514
I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE)							63,139
MTDC (Rate: 51.5000, Base: 51865) TOTAL INDIRECT COSTS (F&A)							
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)							26,710
K. SMALL BUSINESS FEE							89,849
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)							0
M. COST SHARING PROPOSED LEVEL \$ 0							89,849
AGREED LEVEL IF DIFFERENT \$							
PI/PD NAME				FOR NSF USE ONLY			
Detlef Knappe ORG. REP. NAME*				INDIRECT COST RATE VERIFICATION			
		Date Checked		Date Of Rate Sheet		Initials - ORG	

SUMMARY PROPOSAL BUDGET

Cumulative

ORGANIZATION North Carolina State University		PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR Detlef Knappe		AWARD NO.	
PROPOSAL NO.		DURATION (months)		Funds Requested By proposer (if different) NSF	
FOR NSF USE ONLY					

A. SENIOR PERSONNEL: P/PO, Co-PI's, Faculty, and Other Senior Associates (List each separately with title, A.7, show number in brackets)		NSF Funded	ACAD	SUMR	Funds Requested By proposer (if different) NSF
1. Detlef Knappe - PI	0.00	0.00	0.20	2,500	
2.					
3.					
4.					
5.					
6. () OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE)	0.00	0.00	0.00	0	
7. () TOTAL SENIOR PERSONNEL (1 - 6)	0.00	0.00	0.20	2,500	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. () POST DOCTORAL SCHOLARS	0.00	0.00	0.00	0	
2. () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	0.00	0.00	0.00	0	
3. () GRADUATE STUDENTS	24,600				
4. () UNDERGRADUATE STUDENTS	1,000				
5. () SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)	0				
6. () OTHER	0				
TOTAL SALARIES AND WAGES (A + B)					
	28,100				
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)					
	4,525				
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					
	32,625				
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.)					
TOTAL EQUIPMENT					
	0				
E. TRAVEL					
1. DOMESTIC (INCL. U.S. POSSESSIONS)	3,000				
2. FOREIGN	0				
F. PARTICIPANT SUPPORT COSTS					
1. STIPENDS \$	0				
2. TRAVEL	0				
3. SUBSISTENCE	0				
4. OTHER	0				
TOTAL NUMBER OF PARTICIPANTS ()					
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES	10,000				
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION	0				
3. CONSULTANT SERVICES	0				
4. COMPUTER SERVICES	0				
5. SUBAWARDS	0				
6. OTHER	17,514				
TOTAL OTHER DIRECT COSTS					
	27,514				
H. TOTAL DIRECT COSTS (A THROUGH G)					
	63,139				
I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE)					
TOTAL INDIRECT COSTS (F&A)					
	26,710				
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)					
	89,849				
K. SMALL BUSINESS FEE					
	0				
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)					
	89,849				
M. COST SHARING PROPOSED LEVEL \$					
	0				
N. COST SHARING PROPOSED LEVEL IF DIFFERENT \$					
P/PO NAME					
Detlef Knappe					
ORG. REP. NAME					
Date Checked					
Date Of Rate Sheet					
Initials - ORG					

C. ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET

Budget Justification

Salaries

Funds are requested to support Principal Investigator (PI) Knappe for 0.2 summer months. Support for one Graduate Research Assistant (GRA) is requested for 12 months. The GRA will be responsible for sample collection, sample analysis, conducting experiments, and data evaluation. The GRA will work under the direction of the PI. The GRA will earn \$2,050 per month for a 50% appointment. In addition, funds for one undergraduate research assistant (URA) are requested (~10 hours/week for 10 weeks) to support GRA activities.

Fringe Benefits

NCSU faculty fringe benefits (Social Security, retirement, Worker's Compensation, unemployment, health insurance, etc.) are calculated at 30% of total salary. Fringe benefits for the GRA and URA have been calculated at 15% and 8.45% of total salary, respectively.

Materials and Supplies

Supplies (laboratory consumables such as LC columns, analytical standards, mass-labeled internal standards, sample vials, filters, chemicals, and glassware) in the amount of \$10,000 will be needed to conduct the proposed research.

Travel

Travel expenses (\$3,000) are budgeted for (1) sample collection (mileage for in-state travel, car rental from NCSU motor pool) and (2) support of one research team member to attend one national conference to present research results.

Tuition (Included in Other Direct Costs)

Graduate student tuition (\$11,274) was calculated for 1 graduate student at the following rates: \$7,852 in-state tuition + \$3,422 out-of-state tuition support plan. In-state Graduate Assistantship tuition and the Graduate Tuition Remission match (GTRM) has been budgeted for the GRA. The graduate tuition remission match (GTRM, formerly referred to as GSSP) is 25% of the difference between out-of-state and in-state graduate tuition. The current partial non-resident graduate tuition remission is \$3,422 per year. Graduate Student Tuition is calculated using the current In-State tuition rate for 9 Semester hours (full time). The Sponsor pays only the amount budgeted. Please note that the funds for the GTRM supplement will be re-budgeted if not needed to cover a portion of the costs associated with out-of-state tuition.

Laboratory Fees (Included in Other Direct Costs)

The laboratory user fee is \$520 per person per month, and the budget line item is based on the anticipated laboratory activities of one GRA for a period of 12 months. This fee covers general laboratory activity such as service contracts for the water purification system, dish washing, routine chemicals, gases, and scale calibration.

Indirect Costs

The NCSU, federally approved Facilities & Administrative rate of 51.5% (for on-campus research) will be charged on all direct costs, with the exception of: equipment, GRA tuition, and any subcontract amount greater than \$25,000. MTDC = "Modified Total Direct Costs whereby direct charges such as Tuition, Scholarship and Fellowship costs, Equipment greater than \$5,000, and each subcontract budgeted amount beyond \$25,000 are excluded from the basis of computing facilities and administrative costs"



Current and Pending Support

(See GPG Section II.D.8 for guidance on information to include on this form.)

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.	
Investigator: Deter Knappe	Other agencies (including NSF) to which this proposal has been/will be submitted.
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support	
Project/Proposal Title: 1,4-Dioxane in North Carolina Drinking Water Sources: Occurrence and Treatment Options	
Source of Support: North Carolina Urban Water Consortium	
Total Award Amount: \$120,531	
Total Award Period Covered: 6/1/14-5/31/16	
Location of Project: NC State University	
Person-Months Per Year Committed to the Project.	
Cal: Acad: Sumr: 0.5	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support	
Project/Proposal Title: Evaluation of cVOC Removal Efficiencies by Various Technologies	
Source of Support: Arcadis (Prime: Water Research Foundation)	
Total Award Amount: \$105,000	
Total Award Period Covered: 5/15/14-12/31/15	
Location of Project: NC State University	
Person-Months Per Year Committed to the Project.	
Cal: Acad: Sumr: 0.2	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support	
Project/Proposal Title: GAC Control of Regulated and Emerging DBPs of Health Concern	
Source of Support: Hazen & Sawyer (Prime: Water Research Foundation)	
Total Award Amount: \$89,998 (to NCSU)	
Total Award Period Covered: 1/1/15-12/31/16	
Location of Project: NC State University, University of SC (Susan Richardson), CU-Boulder (Scott Summers)	
Person-Months Per Year Committed to the Project.	
Cal: Acad: Sumr: 0.2	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support	
Project/Proposal Title: Development and Evaluation of Colloidal Materials to Adjust Aquifer pH and Enhance Contaminant Biodegradation	
Source of Support: Solutions - IES	
Total Award Amount: \$122,110	
Total Award Period Covered: 01/01/13 - 03/01/17	
Location of Project: NC State University	
Person-Months Per Year Committed to the Project.	
Cal: Acad: Sumr: 0.5	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support	
Project/Proposal Title: Generation of Biodegradation-Sorption Barriers for Munitions Constituents (with Robert Borden, NCSU)	
Source of Support: US Army Corps of Engineers	
Total Award Amount: \$820,000	
Total Award Period Covered: 03/30/11 - 03/30/16	
Location of Project: NC State University	
Person-Months Per Year Committed to the Project.	
Cal: Acad: Sumr: 0.5	
Support: <input checked="" type="checkbox"/> Current <input type="checkbox"/> Pending <input type="checkbox"/> Submission Planned in Near Future <input type="checkbox"/> *Transfer of Support	
Project/Proposal Title: "If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period."	
NSF Form 1239 (10/99)	
USE ADDITIONAL SHEETS AS NECESSARY	

Current and Pending Support

(See GPG Section II.D.8 for guidance on information to include on this form.)

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.

Investigator: Knappe Other agencies (including NSF) to which this proposal has been/will be submitted:
none

Support: ☒ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:

Henry's Law Constants and Freundlich Adsorption Constants for VOCs

Source of Support: Water Research Foundation

Total Award Amount: \$100,000

Total Award Period Covered: 10/01/12-7/1/15

Location of Project: NC State University

Person-Months Per Year Committed to the Project.

Cal: Acad: Sumr: 0.2

Support: ☒ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:

Evaluation of Flocculants: Optimizing Characteristics and Screening Methods (PI: R. McLaughlin, NCSU Soil Science)

Source of Support: NC Department of Transportation

Total Award Amount: \$199,523

Total Award Period Covered: 08/15/14-08/14/16

Location of Project: NC State University

Person-Months Per Year Committed to the Project.

Cal: 1.0 Acad: Sumr:

Support: ☒ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:

RAPID; GOALIE: Sources of 1,4-Dioxane in the Cape Fear River Watershed of North Carolina and Treatment Options for 1,4-Dioxane Control

Source of Support: National Science Foundation

Total Award Amount: \$50,000

Total Award Period Covered: 08/15/14-07/31/15

Location of Project: NC State University

Person-Months Per Year Committed to the Project.

Cal: 0.1 Acad: Sumr:

Support: ☐ Current ☒ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:

EAGER; GOALIE: Perfluoro(poly)ethers – an emerging class of drinking water contaminants

Source of Support: National Science Foundation

Total Award Amount: \$89,849

Total Award Period Covered: 08/15/15-08/14/16

Location of Project: NC State University

Person-Months Per Year Committed to the Project.

Cal: 0.2 Acad: Sumr:

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:

Source of Support:

Total Award Amount:

Total Award Period Covered:

Location of Project:

Person-Months Per Year Committed to the Project.

Cal: Acad: Sumr:

*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

NSF Form 1239 (10/99)

USE ADDITIONAL SHEETS AS NECESSARY



Current and Pending Support

(See GPG Section II.C.2.h for guidance on information to include on this form.)

The following information should be provided for each investigator and other senior personnel. Failure to provide this information may delay consideration of this proposal.

Investigator: Michael Richardson
Other agencies (including NSF) to which this proposal has been/will be submitted.

Support: ☒ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title: No externally funded research projects
Source of Support:
Total Award Amount: \$ 0
Total Award Period Covered: 01/01/00 - 01/01/00
Location of Project:
Person-Months Per Year Committed to the Project. Cal: 0.00 Acad: 0.00 Sumr: 0.00

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:
Source of Support:
Total Award Amount: \$
Total Award Period Covered:
Location of Project:
Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:
Source of Support:
Total Award Amount: \$
Total Award Period Covered:
Location of Project:
Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:
Source of Support:
Total Award Amount: \$
Total Award Period Covered:
Location of Project:
Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:

Support: ☐ Current ☐ Pending ☐ Submission Planned in Near Future ☐ *Transfer of Support
Project/Proposal Title:
Source of Support:
Total Award Amount: \$
Total Award Period Covered:
Location of Project:
Person-Months Per Year Committed to the Project. Cal: Acad: Sumr:

*If this project has previously been funded by another agency, please list and furnish information for immediately preceding funding period.

Facilities and Equipment

The Environmental Engineering Laboratories in the Department of Civil, Construction, and Environmental Engineering at NCSU provide excellent research facilities. We have over 5,000 square feet of laboratory space including special areas and equipment for bench and pilot-scale research on water and wastewater treatment, contaminant transport and site remediation, refuse decomposition, anaerobic microbiology, analytical chemistry, and applied molecular microbial ecology. The laboratory is supervised by a full-time manager.

Specialized equipment applicable to the proposed research includes:

- 5 gas chromatographs (GCs) equipped with thermal conductivity, flame ionization, flame photometric, photoionization and electron capture detectors; the GCs are equipped with purge and trap, headspace, or liquid autosamplers;
- one ion-trap GC-MSⁿ equipped with a CombiPAL liquid, headspace, and SPME autosampler as well as with a purge and trap autosampler;
- 3 high performance liquid chromatographs equipped with conductivity (for ion chromatography), UV-visible, photodiode array, and electrochemical detectors, autosamplers, and a fraction collector;
- 2 TOC analyzers, one with TN capability;
- one Perkin-Elmer Tricarb 2800TR Liquid Scintillation Analyzer;
- one gas adsorption analyzer for the characterization of porous materials (BET surface area, pore size distribution in micropores and mesopores);
- two rotary tumblers for equilibration of batch reactors used in adsorption isotherm experiments
- one ozone generator (Pacific Ozone)
- one collimated beam apparatus equipped with low-pressure UV lamps
- 2 anaerobic chambers;
- refrigeration for sample storage; 3 walk-in temperature control rooms, operated at 4 and 38°C; incubators operating at user-selectable temperatures; and
- one steam fed autoclave.

In addition, the laboratory is well equipped with standard equipment (e.g. pH meters, spectrophotometers, etc.).

Specialized equipment will also be available for the proposed research at the National Exposure and Risk Laboratory (NERL) of the USEPA in Research Triangle Park, NC (see attached support letter) as follows:

- Agilent 1100 liquid chromatograph (LC) coupled with a PE Sciex API 3000 triple quadrupole mass spectrometer
- Waters Acquity ultra high pressure liquid chromatograph (UPLC) system combined with a Quattro Premier(tm) XE triple quadrupole mass spectrometer
- Agilent 1100 LC with an Agilent 1969A MSD time of flight (TOF) mass spectrometer
- Agilent 5973 gas chromatograph/mass spectrometer (GC/MS)
- five Waters positive displacement Sep-Pak Concentrators (used for loading solid phase extraction columns)

Data Management Plan

Roles And Responsibilities

The principal investigator (Knappe) will be responsible for coordinating and assuring data storage and access. At the start of the project, the PI will convene a dedicated data management meeting for all project personnel (co-PI Richardson, NCSU postdoctoral research associate and PhD student, collaborators at US EPA) during which naming, processing, and storage conventions for raw and derivative data are introduced. The PI will ensure that NSF policy regarding data management and dissemination are followed during all stages of the project. No direct cost is associated with the data management plan for this project. The infrastructure to be used for data management of this project already exists at NC State University. The NC State IT infrastructure will be used for all data management related to the proposed research.

Types of Data

Data to be collected in the proposed research are described in the project description. The primary data resulting from the proposed activities are water quality data (concentrations of perfluoroalkyl substances (PFASs) as well as common background water matrix parameters) obtained from the analysis of stream samples, samples from the Sweeney water treatment plant, composited samples of finished drinking water, and distribution system samples. Acceptance criteria for experimental data are based on rigorous QA/QC protocols developed from published EPA methods. The data will be in the form of hand-written notes in laboratory notebooks, raw data files from sample analyses, and experimental analysis data files as follows:

1. Laboratory notebooks: Experimental conditions and observations will be recorded in numbered and dated laboratory notebooks. In addition, certain measurements will be recorded by hand in the laboratory notebooks (e.g. pH, temperature, UV absorbance).
2. Raw data: PFAS data will be captured by software controlling the LC-MS/MS. In addition, some background water quality parameters (e.g. total/dissolved organic carbon) will be captured by instrument software.
3. Experimental analysis data files: Any derivative data (e.g. processed LC-MS/MS data, standard curves) will be developed in Microsoft Excel.

Data Formats And Metadata

Raw data collected by LC-MS/MS and other software-driven instrumentation will be stored in the format specific to the software controlling the instrument. Any derivative data (e.g. standard curves, processed LC-MS/MS data) will be prepared in Microsoft Excel format. All experimental procedures, designs and observations will be clearly described and recorded in dated and numbered laboratory notebooks. Metadata files will be prepared in Excel format and will contain the following information: date data were gathered, the name of the investigator who obtained the data, a short description of the experiment, chromatographic peak areas, standard curves, calculated concentrations, and additional derivative results such as rate constants or adsorption capacities. A detailed description of the data and experimental conditions will be included in an accompanying laboratory notebook description. Metadata will be created as soon as raw data are collected, thus allowing efficient management and rapid sharing of the data with others.

Data Sharing and Access

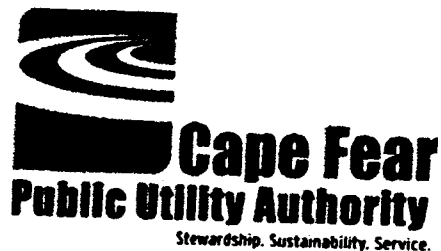
Data generated in the proposed research will be of interest to researchers in the environmental engineering and science communities, water treatment professionals, industries producing or using PFASs, and regulators. All research findings will be disseminated through peer-reviewed journal papers, conference papers, and presentations at conferences and workshops, including seminars at CFPUA. Project-related student dissertations will be made publicly available via the NCSU library website. All raw data will be made freely available by the time of publication or the end of the funding period, consistent with NSF policy.

Data Archiving And Preservation

All raw and derivative data and documentation generated during this grant will be archived at North Carolina State University using existing IT infrastructure. Long-term data storage is available from NC State's Office of Information Technology Shared Services group. Data are stored on a highly scalable, resilient (no single point of failure) storage system. Data are backed up at a data center ~15 miles from the data center where the storage system is located.

Access to data is provided using web servers, ftp servers, or iRODS (Integrated Rule-Oriented Data System) data grid as appropriate for the data types being accessed. Data access servers are provided using virtual servers provisioned in NC State's Virtual Computing Lab (VCL) environment. Utilizing NC State's VCL, various methods of access to the data can be provided based on what is appropriate. Web servers - either centrally managed shared web server or research group managed dedicated web server - providing access using http, https, or ftp protocols or iRODS server providing data grid access are current options available for off campus data access.

No post-doctoral support requested



Dr. Detlef Knappe
North Carolina State University
Department of Civil, Construction, and Environmental Engineering
Campus Box 7908
Raleigh, NC 27695-7908

June 10, 2015

Re: EAGER: GOALI: Perfluoro(poly)ethers - an emerging class of drinking water contaminants

Dear Dr. Knappe,

The purpose of this letter is to confirm that the Cape Fear Public Utility Authority (CFPUA) has a strong interest in collaborating with you and your students on the above referenced research. In my position as the Water Resources Manager at CFPUA, I confirm my participation as a co-principal investigator.

CFPUA's Sweeney water treatment plant (WTP) has a design capacity of 35 mgd and treats water from the Cape Fear River. Apart from conventional water treatment processes, our treatment train includes both raw and settled water ozonation, granular activated carbon (GAC) biofiltration, and UV disinfection. Even with these advanced treatment processes, our results from ongoing sampling for USEPA's third unregulated contaminant monitoring rule (UCMR3) show that unregulated contaminants such as 1,4-dioxane and perfluoroalkyl substances (PFASs) occur in our finished water. In addition, analyses conducted by you and your colleagues at EPA identified new perfluoro(poly)ethers (PFPEs) in the raw and finished water from the Sweeney WTP. CFPUA is concerned about the presence of PFPEs and other unregulated industrial contaminants in our source water, especially because many respond either poorly or not at all to the advanced treatment processes available at the Sweeney WTP. An additional concern of ours is the fate of PFPEs in our aquifer storage and recovery (ASR) system.

CFPUA would like to partner with you to (1) develop analytical methods that will allow us to quantify PFPE concentrations in our source water, (2) measure adsorbable organic fluorine (AOF) to determine what fraction of the AOF is identifiable by targeted LC-MS/MS analysis, (3) assess PFPE removal/transformation in the treatment processes employed at the Sweeney WTP and in our ASR facility, and (4) identify treatment options for PFPE removal from water.

Some ways in which CFPUA will contribute to the proposed research are as follows:

- Host a student from your research group to become familiar with the Sweeney WTP, our ASR facility, and our distribution system. This experience will provide your student with an opportunity to develop sampling plans that will allow us to track water and PFPE fate from our intake location all the way to our customers' taps.
- Closely collaborate with you and your student to study the removal/transformation of PFPEs in full-scale unit processes as well as in our ASR facility.
- Collaborate with you to communicate the results of the study to affected utilities and coordinate efforts between affected utilities, regulatory agencies, and identified sources to eliminate and/or reduce PFPE concentrations in the Cape Fear River to acceptable levels.



Our goal is to closely collaborate with you and your graduate students to facilitate knowledge transfer. If you have any questions, feel free to contact me by email at Michael.richardson@cfpu.org or by phone at 910-332-6723.

Sincerely,
Michael Richardson
Water Resources Manager

235 Government Center Drive, Wilmington, NC 28403
t: 910-799-6064 f: 910-799-6066 www.cfpu.org



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
National Exposure Research Laboratory
Research Triangle Park, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

June 10, 2015

Dr. Detlef Knappe
Department of Civil, Construction, and Environmental Engineering
Campus Box 7908
North Carolina State University
Raleigh, NC 27695-7908

Re: EAGER: GOALIE: Perfluoro(poly)ethers – a new class of drinking water contaminants

Dear Dr. Knappe,

The National Exposure Research Laboratory of the U.S. Environmental Protection Agency enthusiastically supports your proposed NSF grant application and looks forward to collaborating with you in the following manner:

- Train graduate students and post-doctoral research associates to conduct targeted and non-targeted HPLC-MS/MS and TOFMS analysis
- Provide access to our analytical equipment (HPLC-MS/MS and TOFMS)
- Provide consumable materials and reagents necessary for targeted and non-targeted analysis
- Preparation of joint peer-reviewed manuscripts and conference presentations

If you have any questions, please contact me directly using the information provided below.

Sincerely,

A handwritten signature in black ink, which appears to read "Andrew B. Lindstrom", is positioned below the "Sincerely," text.

Andrew B. Lindstrom, Ph.D.
Human Exposure and Atmospheric Sciences Division
National Exposure Research Laboratory
U.S. Environmental Protection Agency
Mail Drop E205-04
Research Triangle Park, NC 27711

Tel: 919-541-0551 Fax: 919-541-3527
Email: Lindstrom.andrew@epa.gov

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Wednesday, August 26, 2015 1:52 PM
To: Jim Flechtner; Leslie Ogilvie; Michael Richardson
Subject: IP Agreement for NSF GOALIE project - Signature needed
Attachments: 15-3259 Knappe GOALI NSF IP Agreement 08-26-2015.pdf

Hi Jim,

In June, I submitted a research proposal to the National Science Foundation to conduct a collaborative project between NCSU and CFPUA.

The goal is to study the fate of perfluorinated ethers in the Cape Fear River from the point of discharge near Fayetteville to your drinking water intake. In addition, we are planning to evaluate the treatment effectiveness of individual unit processes at the Sweeney WTP. Mike is a co-principal investigator on the project.

No money would be exchanged between CFPUA and NCSU or CFPUA and NSF, and I expect that no patentable products will be developed (key points of the attached agreement).

Could you take a look at the attached and let me know if you have questions? If you have questions, please contact me at 919-274-7307. NSF will only fund my research group if I submit the signed form to NSF by this Friday (8/28).

Thank you and best regards,

Detlef

--
Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

**Allocation of Rights In Intellectual Property under the NSF Grant
Opportunities for Academic Liaison with Industry (GOALI) Program**

This Agreement between "Cape Fear Public Utility Authority", having a principal place of business at 235 Government Center Dr. Wilmington, NC 28403 ("COMPANY") and **NORTH CAROLINA STATE UNIVERSITY**, a research institution having a principal place of business at 2701 Sullivan Drive, Suite 240, Administrative Services III, Raleigh, North Carolina, 27613 ("UNIVERSITY") is entered into for the purpose of allocating between the parties certain rights relating to an GOALI project to be carried out by COMPANY and UNIVERSITY (hereinafter referred to as the "PARTIES") under an GOALI funding agreement that may be awarded by the National Science Foundation (NSF) to COMPANY to fund a proposal entitled "EAGER: GOALIE: Perfluoro (poly)ethers - a new class of drinking water contaminants," submitted to NSF by COMPANY on or about June 23, 2015

1. Applicability of this Agreement.

- (a) This Agreement shall be applicable only to matters relating to the GOALI project referred to in the preamble above.
- (b) If a funding agreement for a GOALI project is awarded to UNIVERSITY based upon the GOALI proposal referred to in the preamble above, UNIVERSITY will promptly provide a copy of such funding agreement to COMPANY, and UNIVERSITY will make a subaward to COMPANY if applicable in accordance with the funding agreement, the proposal, and this Agreement. If the terms of such funding agreement appear to be inconsistent with the provisions of this Agreement, the Parties will attempt in good faith to resolve any such inconsistencies. However, if such resolution is not achieved within a reasonable period, UNIVERSITY shall not be obligated to award nor COMPANY to accept the subaward. If a subaward is made by UNIVERSITY and accepted by COMPANY, this Agreement shall not be applicable to contradict the terms of such subaward or of the funding agreement awarded by NSF to UNIVERSITY except on the grounds of fraud, misrepresentation, or mistake, but shall be considered to resolve ambiguities in the terms of the subaward.
- (c) The provisions of this Agreement shall apply to any and all consultants, subcontractors, independent contractors, or other individuals employed by UNIVERSITY or COMPANY for the purposes of this GOALI project.

2. Background Intellectual Property.

- (a) "Background Intellectual Property" means property and the legal right therein of either or both PARTIES developed before or independent of this Agreement including inventions, patent applications, patents, copyrights, trademarks, mask works, trade secrets and any information embodying proprietary data such as technical data and computer software.
- (b) Any agreement for UNIVERSITY Background Intellectual Property that is unencumbered and available for licensing must be negotiated with the UNIVERSITY Office of Technology Transfer.

3. Project Intellectual Property.

- (a) "Project Intellectual Property" means the legal rights relating to inventions (including Subject Inventions as defined in 37 CFR 401), patent applications, patents, copyrights, trademarks, mask works, trade secrets and any other legally protectable information, including computer software, first made or generated during the performance of this GOALI project.

- (b) Except as otherwise provided herein, ownership of Project Intellectual Property shall vest in the party whose personnel conceived the subject matter or first actually reduced the subject matter to practice, and such party may perfect legal protection therein in its own name and at its own expense. Jointly made or generated Project Intellectual Property shall be jointly owned by the Parties unless otherwise agreed in writing. The COMPANY shall have the first option to negotiate for UNIVERSITY's rights in Project Intellectual Property whether solely or jointly made unless otherwise agreed in writing. Inventorship shall be determined in accordance with U.S. Patent laws.

- (c) The Parties agree to disclose to each other, in writing, each and every Subject Invention, which may be patentable or otherwise protectable under the United States patent laws in Title 35, United States Code. The Parties acknowledge that they will disclose Subject Inventions to each other and the NSF within two (2) months after their respective inventor(s) first disclose the invention in writing to the person(s) responsible for patent matters of the disclosing Party. All written disclosures of such inventions shall contain sufficient detail of the invention, identification of any statutory bars, and shall be marked confidential, in accordance with 35 U.S.C. 205.

- (d) Each party hereto may use Project Intellectual Property of the other nonexclusively and without compensation specifically for the research or development activities of this GOALI project, including inclusion in GOALI project reports to the NSF and proposals to the NSF for continued funding of this GOALI project through additional phases.

- (e) In addition to the Government's rights under the Patent Rights clause of 37 CFR 401.14, the Parties agree that the Government shall have an irrevocable, royalty free, nonexclusive license for any governmental purpose in any Project Intellectual Property.

- (f) COMPANY will have an option to commercialize the Project Intellectual Property of UNIVERSITY, subject to any rights of the Government therein, as follows--

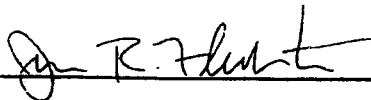
- (1) Where Project Intellectual Property of UNIVERSITY is a potentially patentable invention, provided that COMPANY pays all costs for the preparation, filing, prosecution and maintenance of such Project Intellectual Property, COMPANY will have an exclusive option to negotiate for a license to such invention. The initial option period will be two months after such invention has been reported to COMPANY. COMPANY may, at its election and subject to the patent expense reimbursement provisions of this section, extend such option by up to one month for a total period not to exceed three

AGREED TO AND ACCEPTED BY:

CAPE FEAR PUBLIC UTILITY AUTHORITY

NC STATE UNIVERSITY (UNIVERSITY)

Sign: _____

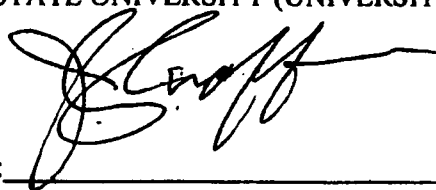


Name: JAMES R. FLECHTNER
Title: EXECUTIVE DIRECTOR

Date: _____

8/26/15

Sign: _____



Name: John Chaffee
Title: Director, Sponsored Programs

Date: Aug 26, 2015

(b) COMPANY will indemnify and hold harmless UNIVERSITY with regard to any claims arising in connection with commercialization of this GOAL project by or under the authority of COMPANY. COMPANY will indemnify and hold harmless the Government with regard to any claims arising in connection with commercialization of the results of this GOAL project.

7. Termination.

(a) This agreement may be terminated by either Party upon thirty (30) days written notice to the other Party. This agreement may also be terminated by either Party in the event of the failure of the other Party to comply with the terms of this agreement.

(b) This agreement shall terminate upon: (i) the execution by both PARTIES of a subcontract contemplated herein that supersedes this Agreement; (ii) the expiration of nine (9) months from the effective date hereof; provided, however, if PROJECT is still under consideration by NSF upon the expiration of the nine (9) month period, this Agreement may be extended upon the mutual agreement of both PARTIES; (iii) failure to obtain NSF's consent to place the subcontract; (iv) judicial determination that either Party is insolvent or bankrupt pursuant to the provisions of any state or federal insolvency law, or the appointed receiver or trustee of the property by reason of either Party's insolvency or inability to pay its debts, or the assignment of substantially all of either Party's property made for the benefit of that Party's creditors; or (v) the mutual agreement of both PARTIES to an effective date of termination.

(c) Nothing in this Agreement shall be construed to create any obligation duty or responsibility to the other party with respect to costs incurred throughout the period of this relationship. Each party is responsible for all their own costs up until the effective date of a Research Agreement between the Parties or the termination of this Agreement. Unless reestablished in a follow-on Research Agreement, Sections 5 and 6 of this Agreement shall survive any termination of this Agreement.

8. Contacts

Any notices required to be given or which may be given under this Agreement must be in writing delivered by private overnight mail service, first-class mail or facsimile addressed to the Parties as follows:

For University:	Office of Sponsored Programs Services North Carolina State University 2701 Sullivan Drive, Suite 240 Campus Box 7514 Raleigh, North Carolina 27695-7514 919-515-2444, sps@ncsu.edu
For Sponsor:	Jim Flechtner Cape Fear Public Utility Authority 235 Government Center Dr. Wilmington, NC 28403 910-332-6669 jim.flechtner@cfpuia.org

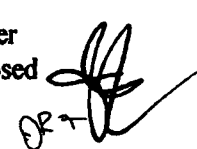
(3) Where more than one royalty might otherwise be due in respect of any unit of product or service under a license pursuant to this Agreement, the parties shall in good faith negotiate to ameliorate any effect thereof that COMPANY can demonstrate would threaten the commercial viability of the affected products or services by providing in such license(s) for the renegotiation of total royalties due in respect of any such unit.

4. Follow-on Research or Development.

All additional research or development work specifically related to the GOALI Project which continues to actively involve both UNIVERSITY and COMPANY, including any licenses, contracts, subcontracts, sublicenses or arrangements of any type, shall contain appropriate provisions to implement the Project Intellectual Property rights provisions of this agreement and insure that the Parties and the Government obtain and retain such rights granted herein in all future resulting research, development, or commercialization work as defined herein.

5. Confidentiality/Publication.

(a) Background Intellectual Property and Project Intellectual Property of a party, as well as other proprietary or confidential information of a party, disclosed by that party to the other in connection with this GOALI project and clearly and properly identified at the time of disclosure as proprietary or confidential shall be received and held in confidence by the receiving party for three years from the date of disclosure and, except with the consent of the disclosing party or as permitted under this Agreement, neither used by the receiving party nor disclosed by the receiving party to others, provided that the receiving party has notice that such information is regarded by the disclosing party as proprietary or confidential. However, these confidentiality obligations shall not apply to use or disclosure by the receiving party after such information is or becomes known to the public without breach of this provision or is or becomes known to the receiving party from a source independent of the disclosing party or is developed by or for the receiving party independently of its disclosure by the disclosing party.

(b) Subject to the terms of paragraph (a) above, either party may publish its results from this GOALI project. However, the publishing party will negotiate the right of refusal with the other party with respect to a proposed publication, as well as a day period in which to review proposed publications and submit comments, which will be given full consideration before publication. Furthermore, upon request of the reviewing party, publication will be deferred for up to 90 additional days for preparation and filing of a patent application which the reviewing party has the right to file or to have filed at its request by the publishing party. 

6. Liability.

(a) Each party disclaims all warranties running to the other or through the other to third parties, whether express or implied, including without limitation warranties of merchantability, fitness for a particular purpose, and freedom from infringement, as to any information, result, design, prototype, product or process deriving directly or indirectly and in whole or part from such party in connection with this GOALI project.

months by giving written notice of such election to UNIVERSITY prior to the expiration of the initial option period. During the period of such option following notice by COMPANY of election to extend, UNIVERSITY will pursue and maintain any patent protection for the invention requested in writing by COMPANY and, except with the written consent of COMPANY or upon the failure of COMPANY to reimburse patenting expenses as required under this section, will not voluntarily discontinue the pursuit and maintenance of any United States patent protection for the invention initiated by UNIVERSITY or of any patent protection requested by COMPANY. For any invention for which COMPANY gives notice of its election to extend the option, COMPANY will, within thirty days after invoice, reimburse UNIVERSITY for the expenses incurred by UNIVERSITY prior to expiration or termination of the option period in pursuing and maintaining any U.S. patent protection initiated by UNIVERSITY and any patent protection requested by COMPANY. COMPANY may terminate such option at will by giving written notice to UNIVERSITY, in which case further accrual of reimbursable patenting expenses hereunder, other than prior commitments not practically revocable, will cease upon UNIVERSITY's receipt of such notice. At any time prior to the expiration or termination of an option, COMPANY may exercise such option by giving written notice to UNIVERSITY, whereupon the parties will promptly and in good faith enter into negotiations for a license under UNIVERSITY's patent rights in the invention for COMPANY to make, use and/or sell products and/or services that embody, or the development, manufacture and/or use of which involves employment of, the invention. The terms of such license will include, inter alia: (i) payment of reasonable royalties to UNIVERSITY on sales of products or services which embody, or the development, manufacture or use of which involves employment of, the invention; (ii) reimbursement by COMPANY of expenses incurred by UNIVERSITY in seeking and maintaining patent protection for the invention in countries covered by the license and, in the case of an exclusive license, (iii) reasonable commercialization milestones and/or minimum royalties.

(2) Where Project Intellectual Property of UNIVERSITY is other than a potentially patentable invention, COMPANY will have an exclusive option for a license, for an option period extending until three months following completion of UNIVERSITY's performance of that phase of this GOAL project in which such Project Intellectual Property of UNIVERSITY was developed by UNIVERSITY. COMPANY may exercise such option by giving written notice to UNIVERSITY, whereupon the parties will promptly and in good faith enter into negotiations for a license under UNIVERSITY's interest in the subject matter for COMPANY to make, use and/or sell products or services which embody, or the development, manufacture and/or use of which involve employment of, such Project Intellectual Property of UNIVERSITY. The terms of such license will include, inter alia: (i) payment of reasonable royalties to UNIVERSITY on sales of products or services that embody, or the development, manufacture or use of which involves employment of, the Project Intellectual Property of UNIVERSITY and, in the case of an exclusive license, (ii) reasonable commercialization milestones and/or minimum royalties.

3. Project Intellectual Property.

- (a) "Project Intellectual Property" means the legal rights relating to inventions (including Subject Inventions as defined in 37 CFR 401), patent applications, patents, copyrights, trademarks, mask works, trade secrets and any other legally protectable information, including computer software, first made or generated during the performance of this GOALI project.
- (b) Except as otherwise provided herein, ownership of Project Intellectual Property shall vest in the party whose personnel conceived the subject matter or first actually reduced the subject matter to practice, and such party may perfect legal protection therein in its own name and at its own expense. Jointly made or generated Project Intellectual Property shall be jointly owned by the Parties unless otherwise agreed in writing. The COMPANY shall have the first option to negotiate for UNIVERSITY's rights in Project Intellectual Property whether solely or jointly made unless otherwise agreed in writing. Inventorship shall be determined in accordance with U.S. Patent laws.
- (c) The Parties agree to disclose to each other, in writing, each and every Subject Invention, which may be patentable or otherwise protectable under the United States patent laws in Title 35, United States Code. The Parties acknowledge that they will disclose Subject Inventions to each other and the NSF within two (2) months after their respective inventor(s) first disclose the invention in writing to the person(s) responsible for patent matters of the disclosing Party. All written disclosures of such inventions shall contain sufficient detail of the invention, identification of any statutory bars, and shall be marked confidential, in accordance with 35 U.S.C. 205.
- (d) Each party hereto may use Project Intellectual Property of the other nonexclusively and without compensation specifically for the research or development activities of this GOALI project, including inclusion in GOALI project reports to the NSF and proposals to the NSF for continued funding of this GOALI project through additional phases.
- (e) In addition to the Government's rights under the Patent Rights clause of 37 CFR 401.14, the Parties agree that the Government shall have an irrevocable, royalty free, nonexclusive license for any governmental purpose in any Project Intellectual Property.
- (f) COMPANY will have an option to commercialize the Project Intellectual Property of UNIVERSITY, subject to any rights of the Government therein, as follows--
 - (i) Where Project Intellectual Property of UNIVERSITY is a potentially patentable invention, provided that COMPANY pays all costs for the preparation, filing, prosecution and maintenance of such Project Intellectual Property, COMPANY will have an exclusive option to negotiate for a license to such invention. The initial option period will be two months after such invention has been reported to COMPANY. COMPANY may, at its election and subject to the patent expense reimbursement provisions of this section, extend such option by up to one month for a total period not to exceed three

**Allocation of Rights In Intellectual Property under the NSF Grant
Opportunities for Academic Liaison with Industry (GOALI) Program**

This Agreement between "Cape Fear Public Utility Authority", having a principal place of business at 235 Government Center Dr. Wilmington, NC 28403 ("COMPANY") and NORTH CAROLINA STATE UNIVERSITY, a research institution having a principal place of business at 2701 Sullivan Drive, Suite 240, Administrative Services III, Raleigh, North Carolina, 27613 ("UNIVERSITY") is entered into for the purpose of allocating between the parties certain rights relating to an GOALI project to be carried out by COMPANY and UNIVERSITY (hereinafter referred to as the "PARTIES") under an GOALI funding agreement that may be awarded by the National Science Foundation (NSF) to COMPANY to fund a proposal entitled "EAGER: GOALIE: Perfluoro (poly)ethers - a new class of drinking water contaminants," submitted to NSF by COMPANY on or about June 23, 2015

1. Applicability of this Agreement.

- (a) This Agreement shall be applicable only to matters relating to the GOALI project referred to in the preamble above.

- (b) If a funding agreement for a GOALI project is awarded to UNIVERSITY based upon the GOALI proposal referred to in the preamble above, UNIVERSITY will promptly provide a copy of such funding agreement to COMPANY, and UNIVERSITY will make a subaward to COMPANY if applicable in accordance with the funding agreement, the proposal, and this Agreement. If the terms of such funding agreement appear to be inconsistent with the provisions of this Agreement, the Parties will attempt in good faith to resolve any such inconsistencies. However, if such resolution is not achieved within a reasonable period, UNIVERSITY shall not be obligated to award nor COMPANY to accept the subaward. If a subaward is made by UNIVERSITY and accepted by COMPANY, this Agreement shall not be applicable to contradict the terms of such subaward or of the funding agreement awarded by NSF to UNIVERSITY except on the grounds of fraud, misrepresentation, or mistake, but shall be considered to resolve ambiguities in the terms of the subaward.

- (c) The provisions of this Agreement shall apply to any and all consultants, subcontractors, independent contractors, or other individuals employed by UNIVERSITY or COMPANY for the purposes of this GOALI project.

2. Background Intellectual Property.

- (a) "Background Intellectual Property" means property and the legal right therein of either or both PARTIES developed before or independent of this Agreement including inventions, patent applications, patents, copyrights, trademarks, mask works, trade secrets and any information embodying proprietary data such as technical data and computer software.
- (b) Any agreement for UNIVERSITY Background Intellectual Property that is unencumbered and available for licensing must be negotiated with the UNIVERSITY Office of Technology Transfer.

--
Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappe-lab.wordpress.ncsu.edu/>

Fax 919.515.7951

laurinda_perez@ncsu.edu

<http://www.engr.ncsu.edu/ora/>

On Mon, Aug 17, 2015 at 10:27 AM, Richardson, Vanessa L. (BFA/DGA) <virichar@nsf.gov> wrote:

Good morning,

Please send the completed signed IP agreement for the project: "EAGER: GOALIE: Perfluoro(poly)ethers - a new class of drinking water contaminants", in accordance with the GOAL solicitation requirements "Grant Opportunities for Academic Liaison with Industry (GOALI) NSF 12-513. <http://www.nsf.gov/pubs/2012/nsf12513/nsf12513.pdf>

Please provide this information by close of business August 24, 2015.

Thank you, and please contact me if you need additional assistance.

Best,

Vanessa L. Richardson

Lead Grant Specialist

Division of Grants and Agreements

National Science Foundation

Arlington, Virginia 22230

virichar@nsf.gov - (703) 292-4839

The only limit to our realization of tomorrow will be our doubts of today. *Franklin D. Roosevelt*

<amburnet@ncsu.edu>; Lenise Sellars <lumpfire@ncsu.edu>; Patrick Hayes <phayes@ncsu.edu>
Subject: Re: CBET - 1550222 - NEED FINAL SIGNED GOALI INTELLECTUAL PROPERTY

Good afternoon Vanessa,

Thank you kindly for your email. I have included the Dept of Civil, Construction and Environmental Engineering and our Office of Sponsored Programs & Regulatory Compliance (SPARCS) in addition to Dr. Knappe (PI) so that they can further assist the PI with this request.

Hello Lenise and SPARCS: This is in relation to Radar 2015-3259/PINS 63566. The deadline to respond is Monday, August 24. Please let me know if you need anything further from the CRO?

Thanks kindly,

Laurinda

Laurinda Perez

Assistant Director of Research Administration

Office of Research & Admin.

College of Engineering

NC State University

21 Current Drive, Rm 115F Page Hall

Campus Box 7901

Raleigh, NC 27695

Phone 919.515.7011

Vanessa,

You are quite welcome. If I can be of further assistance, let me know?

Thanks,

Laurinda

On Mon, Aug 17, 2015 at 1:24 PM, Richardson, Vanessa L. (BFA/DGA) <vlrichar@nsf.gov> wrote:

Thank you so much for your assistance.

Best,

Vanessa L. Richardson

Lead Grants Specialist

Division of Grants and Agreements (DGA)

vlrichar@nsf.gov - (703) 292-4839

From: Laurinda Perez [<mailto:llmarsh@ncsu.edu>]

Sent: Monday, August 17, 2015 1:22 PM

To: Richardson, Vanessa L. (BFA/DGA) <vlrichar@nsf.gov>

Cc: Cooper, William J. <WJCOOPER@nsf.gov>; Knapp, Michael <michael.richardson@cfpa.org>; Young, Jasmine V. <jyoung@nsf.gov>; Richardson, Jessie L

<richard@nsf.gov>; SPS <sp@ncsu.edu>; Rod Lassiter <rod_lassiter@ncsu.edu>; Jalisa Melton

<jmelton@ncsu.edu>; Cynthia Froass <chfroass@ncsu.edu>; Monique Burnette

Burnette <amburnet@ncsu.edu>; Cooper, William J. <WJCOOPER@nsf.gov>; Richardson, Jessie L <lrichard@nsf.gov>; Cynthia Froass <chfroass@ncsu.edu>; Young, Jasmine V. <lyoung@nsf.gov>
Subject: RE: CBET - 1550222 - NEED FINAL SIGNED GOALI INTELLECTUAL PROPERTY

Hi Vanessa,
The IP agreement has now been signed by NCSU and is awaiting signature from CFPUA, our industry partner. The agreement needs to be reviewed by their attorney first. I will forward you the fully executed agreement as soon as I receive it.
Best regards,
Dettef

On Aug 25, 2015 11:00 AM, "Richardson, Vanessa L. (BFA/DGA)" <vrichar@nsf.gov> wrote:
Good morning, all:

Please be advised that this project cannot be forwarded for final review without the final signed IP document. If this is still in progress, please let me know as soon as possible.

Please let me know the status of this process by close of business August 28, 2015, or the program will need to consider selecting another project for funding for FY 2015.

Best,

Vanessa L. Richardson

Lead Grants Specialist

Division of Grants and Agreements (DGA)

vrichar@nsf.gov - (703) 292-4839

From: Laurinda Perez [mailto:llmarsh@ncsu.edu]
Sent: Monday, August 17, 2015 1:28 PM

To: Richardson, Vanessa L. (BFA/DGA) <vrichar@nsf.gov>

Cc: Cooper, William J. <WJCOOPER@nsf.gov>; Knappe@ncsu.edu; michael.richardson@cfpu.org; Laurinda Perez@ncsu.edu; Young, Jasmine V. <lyoung@nsf.gov>; Richardson, Jessie L <lrichard@nsf.gov>; SPS <sps@ncsu.edu>; Rod Lassiter <rod_lassiter@ncsu.edu>; Jalisa Melton <lmelton@ncsu.edu>; Cynthia Froass <chfroass@ncsu.edu>; Monique Burnette <amburnet@ncsu.edu>; Lenise Sellars <lfumphre@ncsu.edu>; Patrick Hayes <phayes@ncsu.edu>
Subject: Re: CBET - 1550222 - NEED FINAL SIGNED GOALI INTELLECTUAL PROPERTY

John Malone

From: Richardson, Vanessa L. (BFA/DGA) <vlrichar@nsf.gov>
Sent: Thursday, August 27, 2015 2:13 PM
To: 'Detlef Knappe'
Cc: Michael Richardson; Patrick Hayes; Jalisa Melton; Rod Lassiter; Laurinda_Perez@ncsu.edu; Lenise Sellars; SPS; Laurinda Perez; Monique Burnette; Cooper, William J.; Richardson, Jessie L; Cynthia Froass; Young, Jasmine V.; Robey, John Christopher
Subject: RE: CBET - 1550222 - NEED FINAL SIGNED GOALI INTELLECTUAL PROPERTY

Thank you all so much for getting this to me so quickly. I am about to forward for final approval.

Best wishes,

Vanessa L. Richardson
Lead Grant and Agreement Specialist
National Science Foundation, Arlington, VA 22230
(703) 292-4839 vlrichar@nsf.gov
I dwell in possibility. ~ Emily Dickinson

From: Detlef Knappe [<mailto:knappe@ncsu.edu>]
Sent: Thursday, August 27, 2015 9:53 AM
To: Richardson, Vanessa L. (BFA/DGA)
Cc: michael.richardson@cfpua.org; Patrick Hayes; Jalisa Melton; Rod Lassiter; Laurinda_Perez@ncsu.edu; Lenise Sellars; SPS; Laurinda Perez; Monique Burnette; Cooper, William J.; Richardson, Jessie L; Cynthia Froass; Young, Jasmine V.
Subject: Re: CBET - 1550222 - NEED FINAL SIGNED GOALI INTELLECTUAL PROPERTY

Hi Vanessa,
In the end, everyone came through quickly. Please see attached.
Let me know if you have questions.
Best,
Detlef

On 8/26/15 3:51 PM, Richardson, Vanessa L. (BFA/DGA) wrote:

Thank you so much. As long as I know that it is coming, I can hold the proposal. Thank you again for your response.

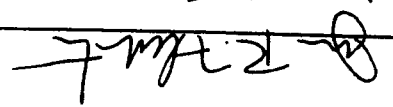
Best,

Vanessa L. Richardson
Lead Grants Specialist
Division of Grants and Agreements (DGA)
vlrichar@nsf.gov - (703) 292-4839

From: Detlef Knappe [<mailto:knappe@ncsu.edu>]
Sent: Wednesday, August 26, 2015 3:24 PM
To: Richardson, Vanessa L. (BFA/DGA) <vlrichar@nsf.gov>
Cc: michael.richardson@cfpua.org; Patrick Hayes <phayes@ncsu.edu>; Jalisa Melton <jmmelton@ncsu.edu>; Rod Lassiter <rod_lassiter@ncsu.edu>; Laurinda_Perez@ncsu.edu; Lenise Sellars <lfumphre@ncsu.edu>; SPS <sps@ncsu.edu>; Laurinda Perez <llmarsh@ncsu.edu>; Monique

AGREED TO AND ACCEPTED BY:

CAPE FEAR PUBLIC UTILITY AUTHORITY NC STATE UNIVERSITY (UNIVERSITY)

Sign: 
Name: JAMES R. FLETCHER
Title: EXECUTIVE DIRECTOR
Date: 8/26/15

Sign: _____
Name: John Chaffee
Title: Director, Sponsored Programs
Date: Aug 26, 2015

[THIS AGREEMENT IS NULL AND VOID UNLESS NEGOTIATED AND SIGNED BY
NC STATE UNIVERSITY'S OFFICE OF SPONSORED PROGRAMS]

- (b) COMPANY will indemnify and hold harmless UNIVERSITY with regard to any claims arising in connection with commercialization of the results of this GOALI project by or under the authority of COMPANY. COMPANY will indemnify and hold harmless the Government with regard to any claims arising in connection with commercialization of the results of this GOALI project.

7. Termination.

- (a) This agreement may be terminated by either Party upon thirty (30) days written notice to the other Party. This agreement may also be terminated by either Party in the event of the failure of the other Party to comply with the terms of this agreement.
- (b) This agreement shall terminate upon: (i) the execution by both PARTIES of a subcontract contemplated herein that supersedes this Agreement; (ii) the expiration of nine (9) months from the effective date hereof; provided, however, if PROJECT is still under consideration by NSF upon the expiration of the nine (9) month period, this Agreement may be extended upon the mutual agreement of both PARTIES; (iii) failure to obtain NSF's consent to place the subcontract; (iv) judicial determination that either Party is insolvent or bankrupt pursuant to the provisions of any state or federal insolvency law, or the appointed receiver or trustee of the property by reason of either Party's insolvency or inability to pay its debts, or the assignment of substantially all of either Party's property made for the benefit of that Party's creditors; or (v) the mutual agreement of both PARTIES to an effective date of termination.
- (c) Nothing in this Agreement shall be construed to create any obligation duty or responsibility to the other party with respect to costs incurred throughout the period of this relationship. Each party is responsible for all their own costs up until the effective date of a Research Agreement between the Parties or the termination of this Agreement. Unless reestablished in a follow-on Research Agreement, Sections 5 and 6 of this Agreement shall survive any termination of this Agreement.

8. Contacts

Any notices required to be given or which may be given under this Agreement must be in writing delivered by private overnight mail service, first-class mail or facsimile addressed to the Parties as follows:

For University:	For Sponsor:
Office of Sponsored Programs Services North Carolina State University 2701 Sullivan Drive, Suite 240 Campus Box 7514 Raleigh, North Carolina 27695-7514 919-515-2444, sps@ncsu.edu	Jim Flechtner Cape Fear Public Utility Authority 235 Government Center Dr. Wilmington, NC 28403 910-332-6669 Jim.Flechtner@cfpua.org

(3) Where more than one royalty might otherwise be due in respect of any unit of product or service under a license pursuant to this Agreement, the parties shall in good faith negotiate to ameliorate any effect thereof that COMPANY can demonstrate would threaten the commercial viability of the affected products or services by providing in such license(s) for the renegotiation of total royalties due in respect of any such unit.

4. Follow-on Research or Development.

All additional research or development work specifically related to the GOALI Project which continues to actively involve both UNIVERSITY and COMPANY, including any licenses, contracts, subcontracts, sublicenses or arrangements of any type, shall contain appropriate provisions to implement the Project Intellectual Property rights provisions of this agreement and insure that the Parties and the Government obtain and retain such rights granted herein in all future resulting research, development, or commercialization work as defined herein.

5. Confidentiality/Publication.

(a) Background Intellectual Property and Project Intellectual Property of a party, as well as other proprietary or confidential information of a party, disclosed by that party to the other in connection with this GOALI project and clearly and properly identified at the time of disclosure as proprietary or confidential shall be received and held in confidence by the receiving party for three years from the date of disclosure and, except with the consent of the disclosing party or as permitted under this Agreement, neither used by the receiving party nor disclosed by the receiving party to others, provided that the receiving party has notice that such information is regarded by the disclosing party as proprietary or confidential. However, these confidentiality obligations shall not apply to use or disclosure by the receiving party after such information is or becomes known to the public without breach of this provision or is or becomes known to the receiving party from a source independent of the disclosing party or is developed by or for the receiving party independently of its disclosure by the disclosing party.

(b) Subject to the terms of paragraph (a) above, either party may publish its results from this GOALI project. However, the publishing party will negotiate the right of refusal with the other party with respect to a proposed publication, as well as a day period in which to review proposed publications and submit comments, which will be given full consideration before publication. Furthermore, upon request of the reviewing party, publication will be deferred for up to 90 additional days for preparation and filing of a patent application which the reviewing party has the right to file or to have filed at its request by the publishing party.

6. Liability.

(a) Each party disclaims all warranties running to the other or through the other to third parties, whether express or implied, including without limitation warranties of merchantability, fitness for a particular purpose, and freedom from infringement, as to any information, result, design, prototype, product or process deriving directly or indirectly and in whole or part from such party in connection with this GOALI project.

[THIS AGREEMENT IS NULL AND VOID UNLESS NEGOTIATED AND SIGNED BY
NC STATE UNIVERSITY'S OFFICE OF SPONSORED PROGRAMS]

months by giving written notice of such election to UNIVERSITY prior to the expiration of the initial option period. During the period of such option following notice by COMPANY of election to extend, UNIVERSITY will pursue and maintain any patent protection for the invention requested in writing by COMPANY and, except with the written consent of COMPANY or upon the failure of COMPANY to reimburse patenting expenses as required under this section, will not voluntarily discontinue the pursuit and maintenance of any United States patent protection for the invention initiated by UNIVERSITY or of any patent protection requested by COMPANY. For any invention for which COMPANY gives notice of its election to extend the option, COMPANY will, within thirty days after invoice, reimburse UNIVERSITY for the expenses incurred by UNIVERSITY prior to expiration or termination of the option period in pursuing and maintaining any U.S. patent protection initiated by UNIVERSITY and any patent protection requested by COMPANY. COMPANY may terminate such option at will by giving written notice to UNIVERSITY, in which case further accrual of reimbursable patenting expenses hereunder, other than prior commitments not practically revocable, will cease upon UNIVERSITY's receipt of such notice. At any time prior to the expiration or termination of an option, COMPANY may exercise such option by giving written notice to UNIVERSITY, whereupon the parties will promptly and in good faith enter into negotiations for a license under UNIVERSITY's patent rights in the invention for COMPANY to make, use and/or sell products and/or services that embody, or the development, manufacture and/or use of which involves employment of, the invention. The terms of such license will include, inter alia,: (i) payment of reasonable royalties to UNIVERSITY on sales of products or services which embody, or the development, manufacture or use of which involves employment of, the invention; (ii) reimbursement by COMPANY of expenses incurred by UNIVERSITY in seeking and maintaining patent protection for the invention in countries covered by the license and, in the case of an exclusive license, (iii) reasonable commercialization milestones and/or minimum royalties.

(2) Where Project Intellectual Property of UNIVERSITY is other than a potentially patentable invention, COMPANY will have an exclusive option for a license, for an option period extending until three months following completion of UNIVERSITY's performance of that phase of this GOALI project in which such Project Intellectual Property of UNIVERSITY was developed by UNIVERSITY. COMPANY may exercise such option by giving written notice to UNIVERSITY, whereupon the parties will promptly and in good faith enter into negotiations for a license under UNIVERSITY's interest in the subject matter for COMPANY to make, use and/or sell products or services which embody, or the development, manufacture and/or use of which involve employment of, such Project Intellectual Property of UNIVERSITY. The terms of such license will include, inter alia,: (i) payment of reasonable royalties to UNIVERSITY on sales of products or services that embody, or the development, manufacture or use of which involves employment of, the Project Intellectual Property of UNIVERSITY and, in the case of an exclusive license, (ii) reasonable commercialization milestones and/or minimum royalties.

3. Project Intellectual Property.

(a) "Project Intellectual Property" means the legal rights relating to inventions (including Subject Inventions as defined in 37 CFR 401), patent applications, patents, copyrights, trademarks, mask works, trade secrets and any other legally protectable information, including computer software, first made or generated during the performance of this GOAL project.

(b) Except as otherwise provided herein, ownership of Project Intellectual Property shall vest in the party whose personnel conceived the subject matter or first actually reduced the subject matter to practice, and such party may perfect legal protection therein in its own name and at its own expense. Jointly made or generated Project Intellectual Property shall be jointly owned by the Parties unless otherwise agreed in writing. The COMPANY shall have the first option to negotiate for UNIVERSITY's rights in Project Intellectual Property whether solely or jointly made unless otherwise agreed in writing. Inventorship shall be determined in accordance with U.S. Patent laws.

(c) The Parties agree to disclose to each other, in writing, each and every Subject Invention, which may be patentable or otherwise protectable under the United States patent laws in Title 35, United States Code. The Parties acknowledge that they will disclose Subject Inventions to each other and the NSF within two (2) months after their respective inventor(s) first disclose the invention in writing to the person(s) responsible for patent matters of the disclosing Party. All written disclosures of such inventions shall contain sufficient detail of the invention, identification of any statutory bars, and shall be marked confidential, in accordance with 35 U.S.C. 205.

(d) Each party hereto may use Project Intellectual Property of the other nonexclusively and without compensation specifically for the research or development activities of this GOAL project, including inclusion in GOAL project reports to the NSF and proposals to the NSF for continued funding of this GOAL project through additional phases.

(e) In addition to the Government's rights under the Patent Rights clause of 37 CFR 401.14, the Parties agree that the Government shall have an irrevocable, royalty free, nonexclusive license for any governmental purpose in any Project Intellectual Property.

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(1) Where Project Intellectual Property of UNIVERSITY is a potentially patentable invention, provided that COMPANY pays all costs for the preparation, filing, prosecution and maintenance of such Project Intellectual Property, COMPANY will have an exclusive option to negotiate for a license to such invention. The initial option period will be two months after such invention has been reported to COMPANY. COMPANY may, at its election and subject to the patent expense reimbursement provisions of this section, extend such option by up to one month for a total period not to exceed three

**Allocation of Rights In Intellectual Property under the NSF Grant
Opportunities for Academic Liaison with Industry (GOALI) Program**

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- (c) The provisions of this Agreement shall apply to any and all consultants, subcontractors, independent contractors, or other individuals employed by UNIVERSITY or COMPANY for the purposes of this GOALI project.

2. Background Intellectual Property.

- (a) "Background Intellectual Property" means property and the legal right therein of either or both PARTIES developed before or independent of this Agreement including inventions, patent applications, patents, copyrights, trademarks, mask works, trade secrets and any information embodying proprietary data such as technical data and computer software.
- (b) Any agreement for UNIVERSITY Background Intellectual Property that is unencumbered and available for licensing must be negotiated with the UNIVERSITY Office of Technology Transfer.

John Malone

From: Jim Flechtner
Sent: Thursday, August 27, 2015 8:17 AM
To: Michael Richardson; knappe@ncsu.edu; Frank Styers; Linda Miles Firm
Subject: IP Agreement for NSF GOALIE Project
Attachments: SKMBT_C36015082708010.pdf

Attached is a copy of the signed agreement. We will be sending a hard copy in today's mail to Dr. Knappe.

This looks like an interesting and valuable study, and I look forward to seeing the findings. Feel free to contact me if I can assist further.

Regards,

Jim

James R. Flechtner, PE
Executive Director
Cape Fear Public Utility Authority
235 Government Center Drive
Wilmington, NC 28403
910-332-6669
Jim.Flechtner@cfpua.org

AGREED TO AND ACCEPTED BY:

CAPE FEAR PUBLIC UTILITY AUTHORITY NC STATE UNIVERSITY (UNIVERSITY)



Sign: _____

Name: _____
Title: _____
Name: John Chaffee
Title: Director, Sponsored Programs

Date: _____
Date: Aug 26, 2015

[THIS AGREEMENT IS NULL AND VOID UNLESS NEGOTIATED AND SIGNED BY
NC STATE UNIVERSITY'S OFFICE OF SPONSORED PROGRAMS]

- (b) COMPANY will indemnify and hold harmless UNIVERSITY with regard to any claims arising in connection with commercialization of the results of this GOALI project by or under the authority of COMPANY. COMPANY will indemnify and hold harmless the Government with regard to any claims arising in connection with commercialization of the results of this GOALI project.

7. Termination.

- (a) This agreement may be terminated by either Party upon thirty (30) days written notice to the other Party. This agreement may also be terminated by either Party in the event of the failure of the other Party to comply with the terms of this agreement.
- (b) This agreement shall terminate upon: (i) the execution by both PARTIES of a subcontract contemplated herein that supersedes this Agreement; (ii) the expiration of nine (9) months from the effective date hereof; provided, however, if PROJECT is still under consideration by NSF upon the expiration of the nine (9) month period, this Agreement may be extended upon the mutual agreement of both PARTIES; (iii) failure to obtain NSF's consent to place the subcontract; (iv) judicial determination that either Party is insolvent or bankrupt pursuant to the provisions of any state or federal insolvency law, or the appointed receiver or trustee of the property by reason of either Party's insolvency or inability to pay its debts, or the assignment of substantially all of either Party's property made for the benefit of that Party's creditors; or (v) the mutual agreement of both PARTIES to an effective date of termination.
- (c) Nothing in this Agreement shall be construed to create any obligation duty or responsibility to the other party with respect to costs incurred throughout the period of this relationship. Each party is responsible for all their own costs up until the effective date of a Research Agreement between the Parties or the termination of this Agreement. Unless reestablished in a follow-on Research Agreement, Sections 5 and 6 of this Agreement shall survive any termination of this Agreement.

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For University:	For Sponsor:
Office of Sponsored Programs Services North Carolina State University 2701 Sullivan Drive, Suite 240 Campus Box 7514 Raleigh, North Carolina 27695-7514 919-515-2444, sps@ncsu.edu	Jim Flechtner Cape Fear Public Utility Authority 235 Government Center Dr. Wilmington, NC 28403 910-332-6669 Jim.Flechtner@cfpua.org

(3) Where more than one royalty might otherwise be due in respect of any unit of product or service under a license pursuant to this Agreement, the parties shall in good faith negotiate to ameliorate any effect thereof that COMPANY can demonstrate would threaten the commercial viability of the affected products or services by providing in such license(s) for the renegotiation of total royalties due in respect of any such unit.

4. Follow-on Research or Development.

All additional research or development work specifically related to the GOALI Project which continues to actively involve both UNIVERSITY and COMPANY, including any licenses, contracts, subcontracts, sublicenses or arrangements of any type, shall contain appropriate provisions to implement the Project Intellectual Property rights provisions of this agreement and insure that the Parties and the Government obtain and retain such rights granted herein in all future resulting research, development, or commercialization work as defined herein.

5. Confidentiality/Publication.

(a) Background Intellectual Property and Project Intellectual Property of a party, as well as other proprietary or confidential information of a party, disclosed by that party to the other in connection with this GOALI project and clearly and properly identified at the time of disclosure as proprietary or confidential shall be received and held in confidence by the receiving party for three years from the date of disclosure and, except with the consent of the disclosing party or as permitted under this Agreement, neither used by the receiving party nor disclosed by the receiving party to others, provided that the receiving party has notice that such information is regarded by the disclosing party as proprietary or confidential. However, these confidentiality obligations shall not apply to use or disclosure by the receiving party after such information is becomes known to the public without breach of this provision or is or becomes known to the receiving party from a source independent of the disclosing party or is developed by or for the receiving party independently of its disclosure by the disclosing party.

(b) Subject to the terms of paragraph (a) above, either party may publish its results from this GOALI project. However, the publishing party will negotiate the right of refusal with the other party with respect to a proposed publication, as well as a day period in which to review proposed publications and submit comments, which will be given full consideration before publication. Furthermore, upon request of the reviewing party, publication will be deferred for up to additional days for preparation and filing of a patent application which the reviewing party has the right to file or to have filed at its request by the publishing party.

6. Liability.

(a) Each party disclaims all warranties running to the other or through the other to third parties, whether express or implied, including without limitation warranties of merchantability, fitness for a particular purpose, and freedom from infringement, as to any information, result, design, prototype, product or process deriving directly or indirectly and in whole or part from such party in connection with this GOALI project.

[THIS AGREEMENT IS NULL AND VOID UNLESS NEGOTIATED AND SIGNED BY
NC STATE UNIVERSITY'S OFFICE OF SPONSORED PROGRAMS]

months by giving written notice of such election to UNIVERSITY prior to the expiration of the initial option period. During the period of such option following notice by COMPANY of election to extend, UNIVERSITY will pursue and maintain any patent protection for the invention requested in writing by COMPANY and, except with the written consent of COMPANY or upon the failure of COMPANY to reimburse patenting expenses as required under this section, will not voluntarily discontinue the pursuit and maintenance of any United States patent protection for the invention initiated by UNIVERSITY or of any patent protection requested by COMPANY. For any invention for which COMPANY gives notice of its election to extend the option, COMPANY will, within thirty days after invoice, reimburse UNIVERSITY for the expenses incurred by UNIVERSITY prior to expiration or termination of the option period in pursuing and maintaining any U.S. patent protection initiated by UNIVERSITY and any patent protection requested by COMPANY. COMPANY may terminate such option at will by giving written notice to UNIVERSITY, in which case further accrual of reimbursable patenting expenses hereunder, other than prior commitments not practically revocable, will cease upon UNIVERSITY's receipt of such notice. At any time prior to the expiration or termination of an option, COMPANY may exercise such option by giving written notice to UNIVERSITY, whereupon the parties will promptly and in good faith enter into negotiations for a license under UNIVERSITY's patent rights in the invention for COMPANY to make, use and/or sell products and/or services that embody, or the development, manufacture and/or use of which involves employment of, the invention. The terms of such license will include, inter alia,: (i) payment of reasonable royalties to UNIVERSITY on sales of products or services which embody, or the development, manufacture or use of which involves employment of, the invention; (ii) reimbursement by COMPANY of expenses incurred by UNIVERSITY in seeking and maintaining patent protection for the invention in countries covered by the license and, in the case of an exclusive license, (iii) reasonable commercialization milestones and/or minimum royalties.

(2) Where Project Intellectual Property of UNIVERSITY is other than a potentially patentable invention, COMPANY will have an exclusive option for a license, for an option period extending until three months following completion of UNIVERSITY's performance of that phase of this GOALI project in which such Project Intellectual Property of UNIVERSITY was developed by UNIVERSITY. COMPANY may exercise such option by giving written notice to UNIVERSITY, whereupon the parties will promptly and in good faith enter into negotiations for a license under UNIVERSITY's interest in the subject matter for COMPANY to make, use and/or sell products or services which embody, or the development, manufacture and/or use of which involve employment of, such Project Intellectual Property of UNIVERSITY. The terms of such license will include, inter alia,: (i) payment of reasonable royalties to UNIVERSITY on sales of products or services that embody, or the development, manufacture or use of which involves employment of, the Project Intellectual Property of UNIVERSITY and, in the case of an exclusive license, (ii) reasonable commercialization milestones and/or minimum royalties.

John Malone

From: Michael Richardson
Sent: Tuesday, May 03, 2016 2:57 PM
To: Ben Kearns
Subject: FW: Beginnings of a paper on perfluoroether carboxylic acids
Attachments: ESTL outline_0503.docx

FYI - Please review and let's discuss before I respond back the Dr. Knappe.

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Tuesday, May 03, 2016 2:26 PM
To: Michael Richardson
Subject: Beginnings of a paper on perfluoroether carboxylic acids

Good afternoon, Mike,

I hope you are doing well. I wanted to share with you the beginnings of a paper we are writing on the occurrence of perfluoroalkyl substances, including the recently discovered perfluoroether carboxylic acids, in the Cape Fear River. The paper includes occurrence data at the intakes of three communities (labeled A, B, and C), including data at the Sweeney intake (community C). We are also including data to show the lack of removal of these compounds across unit processes at Sweeney. We would like to invite you as a co-author to recognize your contributions in collecting composite samples for us and providing us with the opportunity to collect samples at Sweeney. Could you review the attached and give me your feedback? Also, please let me know if you would like to be included as a co-author. In either case, we will keep you in the loop as we develop the paper further.

BTW, my new student Hillary Stoll is further developing the analytical method for these compounds and is planning to begin her sampling campaigns this summer for our current NSF project, on which you are a co-principal investigator. Once the semester winds down a bit, it would be good for us to come down to Wilmington, give you an update, and explore further sampling campaigns at your plant and in your distribution system.

Best,
Detlef

--
Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Tuesday, May 03, 2016 2:26 PM
To: Michael Richardson
Subject: Beginnings of a paper on perfluoroether carboxylic acids
Attachments: ESTL outline_0503.docx

Good afternoon, Mike,

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Best,
Detlef

--
Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Traditional and emerging perfluoroalkyl substances in the Cape Fear River Watershed, North Carolina: Occurrence and fate during conventional and advanced water treatment processes

Abstract

Because of their persistence, bioaccumulation potential, and (eco)toxicity, long-chain perfluoroalkyl substances (PFASs) such as perfluorooctanoic acid and perfluorooctane sulfonate are being replaced with short-chain PFASs and fluorinated alternatives. Limited information is available on the occurrence and behavior of these replacement chemicals. The aim of this study was to investigate (1) the occurrence of traditional and emerging PFASs in the Cape Fear River watershed of North Carolina, USA, (2) their fate through a full-scale water treatment plant, and (3) the effectiveness of powered activated carbon (PAC) for their removal by adsorption. In addition to seven perfluorocarboxylic acids (PFCAs) and three perfluorosulfonic acids (PFSAs), seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs) were studied by liquid chromatography-tandem mass spectrometry (LC-MS/MS). At three surface water intakes, 238 surface water samples were collected from June to November 2013. Concentrations of individual PFCAs and PFSAs reached levels of up to 346 ng/L. Downstream of a PFAS manufacturing site, seven PFECAs were detected. The only PFECA for which an authentic standard was available for quantification, perfluoro-2-propoxypropanoic acid (trade name "GenX"), was detected at an average concentration of 631 ng/L, a level that was approximately five times that of the average summed PFCA and PFSAs concentrations (129 ng/L). The remaining PFECAs, were detected but not quantified due to the lack of authentic standards. Among the PFECAs, three exhibited large chromatographic peak areas (up to 15 times the GenX peak area), suggesting possible high concentrations of these emerging compounds. Analysis of samples collected along the treatment train of a drinking water treatment plant with an intake on the Lower Cape Fear River illustrated that neither traditional nor emerging PFASs were removed during coagulation/flocculation/sedimentation, raw and settled water ozonation, biological activated carbon filtration, or disinfection by medium pressure ultraviolet lamps and free chlorine. The adsorption of PFASs by PAC was evaluated with Cape Fear River water samples collected downstream of the PFAS manufacturing facility. Batch tests were conducted with a thermally activated wood-based PAC at doses of 30, 60 and 100 mg/L. The adsorbability of PFASs increased with increasing chain length. PFSAs exhibited a higher affinity for PAC than PFCAs with the same chain length. Replacing one CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC, such that mono-ethers of a given chain length have a lower affinity than the corresponding PFCA, but the replacement of additional CF_2 groups with ether oxygen groups did not result in additional affinity changes among the studied PFECAs.

Table S11 PFASs detected in the CFR watershed

Compound	Formula	Structure	CAS#	Chain length*
Perfluorocarboxylic acids (PFCA)s				
Perfluorobutanoic acid (PFBA)	C ₄ HF ₉ O ₂	CF ₃ (CF ₂) ₃ COOH	375-22-4	4
Perfluoropentanoic acid (PFPeA)	C ₅ HF ₁₀ O ₂	CF ₃ (CF ₂) ₃ COOH	2706-90-3	5
Perfluorohexanoic acid (PFHxA)	C ₆ HF ₁₁ O ₂	CF ₃ (CF ₂) ₃ COOH	307-24-4	6
Perfluoroheptanoic acid (PFHpA)	C ₇ HF ₁₃ O ₂	CF ₃ (CF ₂) ₃ COOH	375-85-9	7
Perfluorooctanoic acid (PFOA)	C ₈ HF ₁₅ O ₂	CF ₃ (CF ₂) ₃ COOH	335-67-1	8
Perfluorononanoic acid (PFNA)	C ₉ HF ₁₇ O ₂	CF ₃ (CF ₂) ₃ COOH	375-95-1	9
Perfluorodecanoic acid (PFDA)	C ₁₀ HF ₁₉ O ₂	CF ₃ (CF ₂) ₃ COOH	335-76-2	10
Perfluorosulfonic acids (PFSA)s				
Perfluorobutane sulfonic acid (PFBS)	C ₄ HF ₉ SO ₃	CF ₃ (CF ₂) ₃ SOH	29420-49-3	5
Perfluorohexane sulfonic acid (PFHxS)	C ₆ HF ₁₃ SO ₃	CF ₃ (CF ₂) ₃ SOH	355-46-4	7
Perfluorooctane sulfonic acid (PFOS)	C ₈ HF ₁₇ SO ₃	CF ₃ (CF ₂) ₃ SOH	111873-33-7	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)				
Perfluoro-2-methoxyacetic acid (PFMOAA)	C ₃ HF ₅ O ₃	CF ₃ OCF ₂ COOH	674-13-5	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	C ₄ HF ₇ O ₃	CF ₃ O(CF ₂) ₂ COOH	377-73-1	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)	C ₅ HF ₉ O ₃	CF ₃ O(CF ₂) ₂ COOH	863090-89-5	6
Perfluoro-2-propoxypropanoic acid (PFPrOPrA or "GenX")	C ₆ HF ₁₁ O ₃	CF ₃ (CF ₂) ₂ OCF(CF ₃)COOH	13252-13-6	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)				
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	C ₆ HF ₉ O ₄	CF ₃ (OCF ₂) ₂ COOH	39492-88-1	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	C ₇ HF ₁₁ O ₄	CF ₃ (OCF ₂) ₂ COOH	39492-89-2	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	C ₈ HF ₁₃ O ₄	CF ₃ (OCF ₂) ₂ COOH	39492-90-5	10

* Number of carbon (including branched), ether oxygen, and sulfur atoms were added to calculate the chain length.

Commented [DK1]: Add a column for QL? Would be N/A for most others

Commented [MS2R1]: Can't do that while keeping the table in the same page. Will see later if they can fit in the materials and methods section

Commented [DK3R1]: OK. Or a separate table for the analytical method that can go into the SI. That table could include information about Q-ions, IS used for quantification, etc.

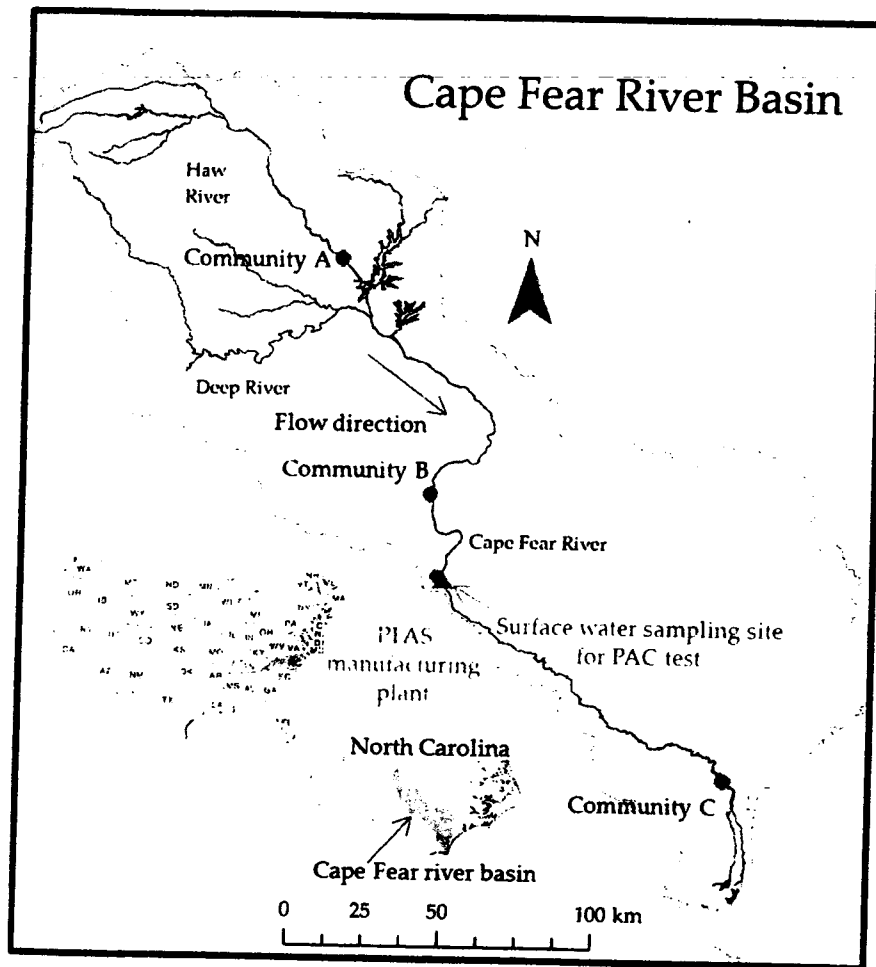


Figure S1. Sampling sites in Cape Fear River watershed, North Carolina

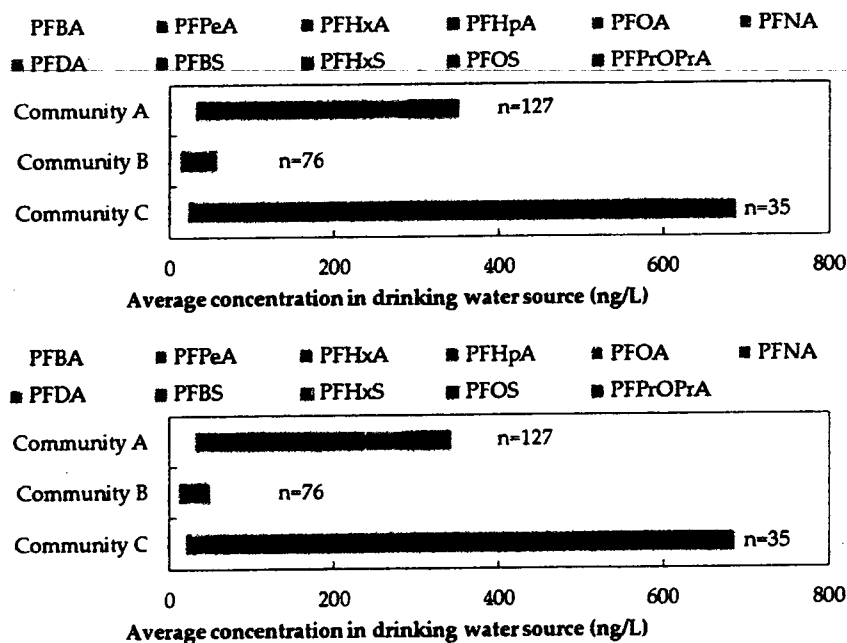


Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and November 2013. Results below the QL were considered as QL/2 (or zero) when calculating averages. Average concentrations less than QL were not plotted. // analyzed by direct injection

- PFASs were detected at surface intakes of three public water systems in the CFR watershed
- In communities A and B, only traditional PFASs were detected (average Σ PFASs at 389 ng/L in community A, and 117 ng/L at community B). The concentrations in community B were lower as a result of dilution by tributaries. One or more important PFAS sources located upstream of community A's intake.
- Max PFOS concentration in community A was above the USEPA drinking water Provisional Health Advisory levels (200 ng/L) on 12 consecutive days during the 127 day sampling. Mean and median concentrations were 49 and 29 ng/L, respectively.
- Mean PFOA concentration in community A (46 ng/L) above New Jersey's guideline to be protective against chronic PFOA exposure (40 ng/L).

Commented [MS4]: The upper figure uses QL/2 for <QL and the lower figure uses zero for <QL in calculating the mean, but not much difference. If the mean is <QL, it is not plotted in either figure.

Commented [DK3R4]: Let's leave both in so Mark and Andy can also comment

- In community C (downstream of a PFAS manufacture site), high concentrations of PFPrOPrA were detected (up to an estimated 4560 ng/L), suggesting the necessity of incorporating emerging PFASs into monitoring. Mean and median concentrations of PFPrOPrA were an order of magnitude higher than those for traditional PFASs in community A. PFPrOPrA concentrations beyond the upper limit of the calibration curve (750 ng/L) were estimated through extrapolation (6 of the 35 samples).

Table S2. Maximum, minimum, mean and median concentrations* (ng/L) of PFASs in CFR watershed surface water as drinking water sources.

Commented [M56]: The upper table assigned QL/2 to all compound concentration <QL, and the lower table assigned 0. I left the sum line there for reference but could remove in later version.

	Community A				Community B				Community C			
	max	min	median	mean	max	min	median	mean	max	min	median	mean
PFBA	99	<10	26	33	38	<10	12	14	104	<10	12	24
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	37
PFHxA	318	<10	48	79	42	<10	<10	13	24	<10	<10	<10
PFHpA	324	<10	39	68	85	<10	<10	14	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	16	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	49	43	<25	<25	<25	40	<25	<25	<25
PFPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
Σ PFASs**	1519	83	241	389	217	70	101	117	4560	55	304	631

* Concentrations < QL were considered as QL/2 to calculate means and Σ PFASs.

** Other PFECAs were present in water samples from community C but could not be quantified and were therefor not included in Σ PFASs

	Community A				Community B				Community C			
	max	min	median	mean	max	min	median	mean	max	min	median	mean
PFBA	99	<10	26	33	38	<10	12	12	104	<10	12	22
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	36
PFHxA	318	<10	48	78	42	<10	<10	11	24	<10	<10	<10
PFHpA	324	<10	39	67	85	<10	<10	11	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	14	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	44	43	<25	<25	<25	40	<25	<25	<25
PFPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
Σ PFASs**	1502	18	212	355	189	0	47	62	4560	55	304	631

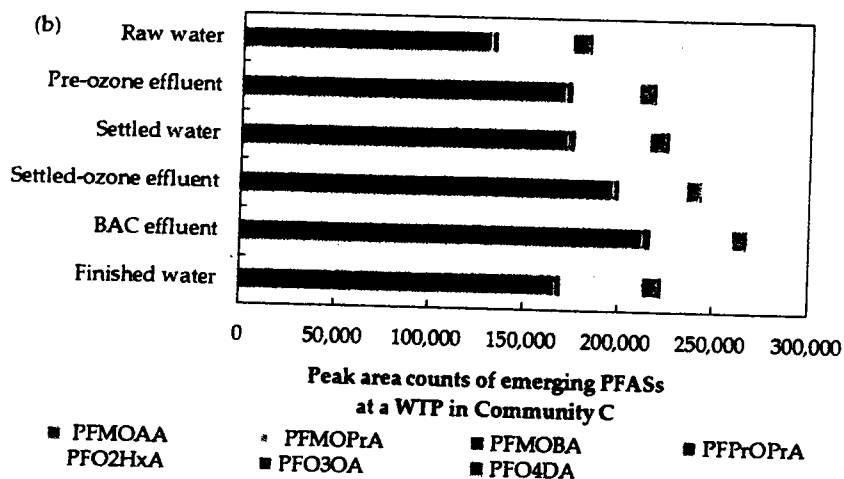
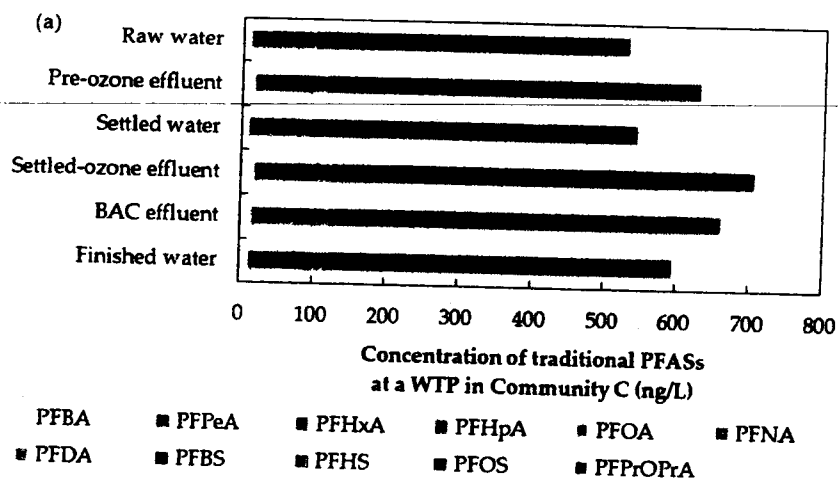


Figure 2. Fate of (a) traditional PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Due to the lack of authentic standards, the emerging PFASs are shown as chromatographic peak area counts from LC-MS/MS analyses. PFPrOPrA data are shown in both figures for reference. Compounds with concentration less than QL were not plotted. // by SPE - UPLC

Commented [M57]: The only problem of doing that is all PFOS concentrations are slightly below 25 ng/L except after ozone. Now by removing all <25 values, it looks as if PFOS didn't exist initially but was generated by the ozone treatment...

Commented [DK87]: We can explain in the text or caption

- Conventional and several advanced drinking water treatment processes (raw and settled water ozonation, biological activated carbon (BAC) filtration, medium pressure UV disinfection) remove neither traditional PFASs nor fluorinated alternatives
- Ozone may lead to an increase in PFCAs, PFSAs, PFMOPrA, PFPrOPrA and PFMOAA concentrations. UV disinfection may decrease concentrations of PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA
- PFPrOPrA is present in both raw and finished water at concentrations that greatly exceeds those of traditional PFASs
- Compared to PFPrOPrA, areas counts for three PFECAs (PFMOAA, PFO2HxA and PFO3OA) were substantially higher.

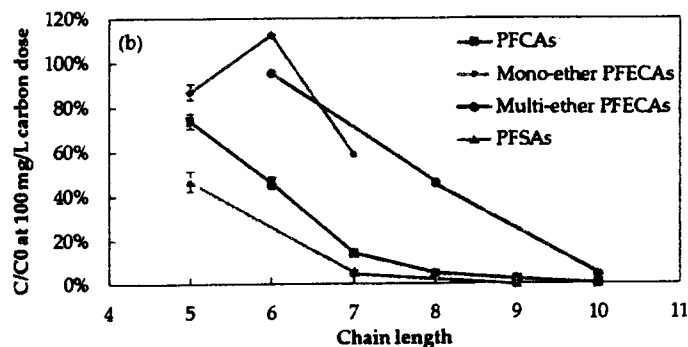
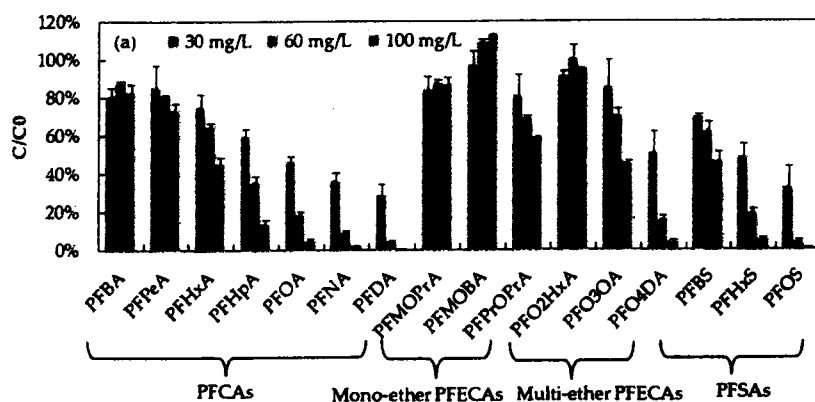


Figure 3. PFAS adsorption to PAC from CFR water after a PAC contact time of 1 hour: fraction remaining (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a function of PFAS chain length. Traditional PFASs were spiked at ~500 ng/L and the emerging PFASs were at their native concentrations. The chart shows the average of remaining PFAS percentage and the error bars show one standard deviation. // by direct injection

- Removals >80% can be achieved with a PAC dose of 100 mg/L for traditional PFCAs with carbon chain length ≥ 7 and with a PAC dose of 60 mg/L carbon for traditional PFCAs with carbon chain length ≥ 8
- At a dose of 100 mg/L, PAC removed 95% of PFO4DA, 54% of PFO3O3, but less than 40% of other PFECAs.
- Adsorbability of both traditional and emerging PFASs increases with increasing chain length
- PFASs were more readily removed than PFCAs of matching chain length
- Replacing one CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC, such that mono-ethers of a given chain length have a lower affinity than the corresponding PFCA (e.g. PFHxA vs. PFMOBA). However, the replacement of additional CF_2 groups with ether oxygen groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA vs. PFO2HxA)
- PFCAs have higher affinity to PACs than mono-ether PFECAs with the same number of perfluorinated carbons (e.g., PFPeA vs. PFMOBA), but lower affinity than multi-ether PFECAs with the same number of perfluorinated carbons (e.g., PFPeA vs. PFO3OA)

John Malone

From: Ben Kearns
Sent: Wednesday, September 07, 2016 4:29 PM
To: knappe@ncsu.edu
Cc: Michael Richardson
Subject: Treatment Question

See Notes in Orange:

Ben Kearns

Surface Water Operations Supervisor

CFPUA Sweeney WTP

235 Government Center Drive

Wilmington, NC 28403

Office: 910-332-6577

Cell: 910-398-4311



Hi Mike and Ben,

On August 18, 2014, we collected water samples after each treatment step in your plant and measured 1,4-dioxane and perfluorinated compound removal in your plant. For this day do you have the following:

1. Raw water ozone dose 3.1 ppm
2. Raw water TOC 6.0 mg/L
3. Coagulant type and dose Aluminum Sulfate – 43 ppm
4. Coagulation pH 5.70 units – average for all three basins that day.
5. Settled water ozone dose 1.3 ppm
6. Settled water TOC 1.90 mg/L
7. Empty bed contact time in GAC biofilters (or filter media depth and hydraulic loading rate for that day)
 - Filter Area = 15 ft wide x 29 ft long
 - Media Depth = 4 ft GAC Media, 12 inches Sand, 12 inches Gravel
 - Flow Rate on Sample Date = 2.00 MGD
8. Medium pressure UV dose 25 mj/cm²

Thank you,

Detlef

--
Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

John Malone

From: Michael Richardson
Sent: Monday, August 15, 2016 2:27 PM
To: Detlef Knappe
Subject: RE: plans

Ben.kearns@cfpua.org and his direct # is 910-332-6577.

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, August 15, 2016 2:24 PM
To: Michael Richardson
Subject: Re: plans

What is his email address?

On 8/15/16 2:23 PM, Michael Richardson wrote:

• Ben Kearns would be the best to contact for now.

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, August 15, 2016 1:39 PM
To: Michael Richardson
Subject: Re: plans

Well deserved, Mike! Who can I contact in the future when we want to work with Sweeney or the NF plant?

Best,

Detlef

On 8/15/16 10:35 AM, Michael Richardson wrote:

Just wanted to let you know that I will be retiring from CFPUA no later than 30SEP2016. I have no immediate plans for the future other than Ava and I will be relocating to our Dunn home as our permanent address most likely before the holiday season this year. We will be putting the Leland home on the market asap.

I have been here for almost 24 years and have been in water treatment for over 40 years. It is time to slow down, relax and enjoy the family as well as see what else life may have to offer for me.

You can reach me by my personal cell phone at 910-617-1757 after the Sept 30th or my personal email mikeeava@bellsouth.net.

Michael E. Richardson
Water Resources Manager
Cape Fear Public Utility Authority
235 Government Center Drive
Wilmington, NC 28403
Direct - 910.332.6723
Cell - 910.470.3009
Chairman, NCWaterWARN

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering
North Carolina State University
Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
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Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Sunday, September 18, 2016 12:06 PM
To: Ben Kearns; Michael Richardson; Mick Noland; Chad Ham; Adam Pickett
Subject: Manuscript on perfluorinated compounds for your review
Attachments: ESTL_0918.docx; ESTL_SI_0918.docx

MANUSCRIPT
FOR REVIEW
TO BEN
&
MIK

Gentlemen,

My research group and EPA colleagues at RTP have drafted the attached manuscript for submission to Environmental Science and Technology Letters. We plan to submit in the week of September 26. The manuscript includes occurrence data for perfluorinated compounds from each of your treatment plants (raw water quality data for all three, and process performance data and finished water quality for Sweeney in Wilmington). We do not name communities, but it would not be difficult for a reader to figure out the names of the three communities. Please let me know whether you have any comments by COB on 9/23.

Thank you,

Detlef

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Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

1 Legacy and emerging perfluoroalkyl substances in the Cape Fear
2 River Watershed of North Carolina: Occurrence and fate during
3 conventional and advanced water treatment processes

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5 Mei Sun^{1,2,*}, Elisa Arevalo², Mark Strynar³, Andrew Lindstrom³, and Detlef R.U. Knappe²

6 ¹Department of Civil and Environmental Engineering

7 University of North Carolina at Charlotte

8 Charlotte, North Carolina 28223, USA

9
10 ²Department of Civil, Construction, and Environmental Engineering

11 North Carolina State University

12 Raleigh, North Carolina 27695, USA

13
14 ³National Exposure Research Laboratory

15 U.S. Environmental Protection Agency

16 Research Triangle Park, North Carolina 27711, USA

17
18 *Corresponding Author Email: msun8@uncc.edu

Abstract

Long-chain perfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten traditionally studied PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) occurrence in the Cape Fear River (CFR) watershed, (2) fate in drinking water treatment processes, and (3) adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in the raw water of a drinking water treatment plant (DWTP), but concentrations of traditionally studied PFASs were high. The US Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctane sulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L (n=37). Six other PFECAs were detected with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. PFAS adsorbability on PAC increased with increasing chain length. Replacing one CF₂ group with an ether oxygen decreased PFAS affinity for PAC, while replacement of additional CF₂ groups with ether oxygens did not lead to further affinity changes.

37 Introduction

38 Perfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain
39 repellents, firefighting foams and food-contact paper coatings. The widespread occurrence of
40 PFASs in drinking water sources is closely related to the presence of industrial sites, military
41 fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain
42 PFASs, such as perfluorocarboxylic acids (PFCAs) with 7 or more carbon atoms and
43 perfluorosulfonic acids (PFSAs) with 6 or more carbon atoms, were predominantly used.²
44 Accumulating evidence about ecotoxicological and human health effects^{3, 4} associated with
45 exposure to long-chain PFASs has led to increased regulatory attention. Recently the U.S.
46 Environmental Protection Agency (USEPA) established a lifetime health advisory level (HAL)
47 of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid
48 (PFOS) concentrations in drinking water.^{5, 6} Over the last decade, production of long-chain
49 PFASs has declined in Europe and North America, and manufactures are moving towards
50 short-chain PFASs and fluorinated alternatives.⁷⁻¹⁰ Some fluorinated alternatives were recently
51 identified,^{8, 11} but the majority of the organofluorine loading to the aquatic environment remains
52 unidentified.¹²⁻¹⁴

53 One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was
54 recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing
55 facility.¹¹ Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-
56 methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-
57 2-propoxypropanoic acid (PFPrOPrA), perfluoro(3,5-dioxahexanoic) acid (PFO2HxA),
58 perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA) and perfluoro(3,5,7,9-tetraoxadecanoic) acid
59 (PFO4DA) (Table S1 and Figure S1 in supporting information (SI)). The ammonium salt of
60 PFPrOPrA is a known PFOA alternative that has been produced since 2010 with the trade name
61 "GenX".¹⁵ According to the manufacturer, the ether oxygen enables "very rapid
62 bioelimination"¹⁵; however, except for the PFPrOPrA data reported by the manufacturer,¹⁶⁻¹⁸
63 little information is available on pharmacokinetic behavior, toxicity, or environmental fate and

transport of PFECAs. To the knowledge of the authors, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,¹⁹ and no published data are available on the fate of PFECAs during water treatment.

The strong C-F bond makes PFASs refractory to abiotic and biotic degradation,²⁰ and most water treatment processes are ineffective for legacy PFAS removal.²¹⁻²⁶ Processes capable of removing PFCAs and PFSAAs include nanofiltration,²⁷ reverse osmosis²⁴, ion exchange,^{27, 28} and activated carbon adsorption,^{27, 28} with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were to (1) identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) evaluate PFAS adsorbability by powdered activated carbon (PAC).

Materials and Methods

Water samples: Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2 in SI). Samples were collected from the raw water tap at each DWTP daily as either 8-hour composite (DWTP A, 127 samples) or 24-hour composite (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250-mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until analysis (within 1 week of receiving). On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train (raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, disinfection by medium pressure UV lamps and free chlorine). Operational conditions of DWTP C on the sampling day are listed in Table S2 in SI. Samples were collected in 1-L HDPE bottles and stored at room temperature until analysis. On the same day, grab samples of CFR water were collected in six 20-L HDPE

89 carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and
90 stored at 4°C until use in PAC adsorption experiments.

91 **Adsorption experiments:** PFAS adsorption by PAC was studied in batch reactors (amber glass
92 bottles, 0.45 L CFR water). PFECAs adsorption was studied at ambient concentrations (~1,000
93 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs ~10-800% of the PFPrOPrA
94 area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water
95 at ~1000 ng/L each. Background water matrix characteristics are summarized in Table S3 in SI.
96 A thermally-activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus OH, mean
97 diameter: 12 µm, BET surface area: 1460 m²/g)²⁹ proved effective for PFAS removal in a prior
98 study²⁸ was used at doses of 30, 60 and 100 mg/L. These doses represent the upper feasible end
99 for drinking water treatment. Samples were taken prior to and periodically after PAC addition
100 for PFAS analysis.

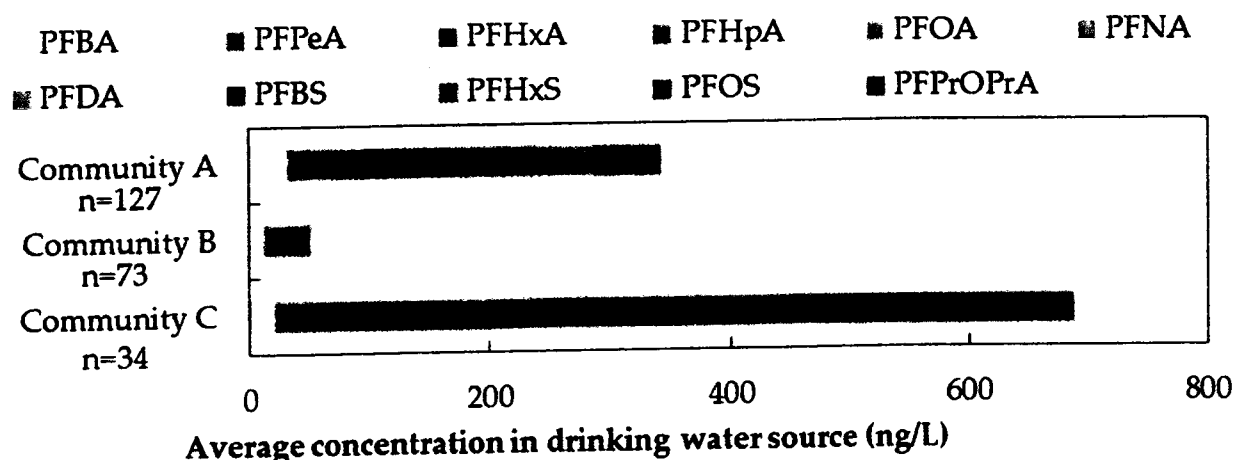
101 **PFAS analysis:** Information about analytical standards and the liquid chromatography-tandem
102 mass spectrometry (LC-MS/MS) method for PFAS quantification is provided in SI.

103 Results and Discussion

104 **PFAS occurrence in drinking water sources:** Mean PFAS concentrations in source water of
105 three DWTPs treating surface water from the CFR watershed are shown in Figure 1. In
106 communities A and B, only legacy PFASs were detected (mean ΣPFAS: 355 ng/L in community
107 A, 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3 in
108 SI. In community A, PFCAs with 4-8 carbons, perfluorohexane sulfonic acid (PFHxS) and PFOS
109 were detected at median concentrations > QLs. Mean and median concentrations were 44 and 29
110 ng/L, respectively, for PFOS, and 46 and 34 ng/L, respectively, for PFOA. During the 127-day
111 sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70
112 ng/L on 57 days, and the mean over the entire study period was 90 ng/L. Similar legacy PFAS
113 concentrations were observed in the same area ten years ago,³⁰ suggesting that PFAS source(s)
114 upstream of community A have long-term negative impacts on drinking water quality. Relating

115 total PFAS concentration to average daily stream flow (Figure S4 in SI) illustrated a general
 116 trend of low PFAS concentrations at high flow and high concentrations at low flow, consistent
 117 with the hypothesis of upstream point source(s). In community B, perfluorobutanoic acid
 118 (PFBA) and perfluoropentanoic acid (PFPeA) were the most frequently detected, with mean
 119 concentrations of 12 and 19 ng/L, respectively. Mean and median PFOA and PFOS
 120 concentrations were <QL, and the maximum sum concentration of PFOA and PFOS was 59
 121 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by
 122 the absence of substantive PFAS sources between the two communities, dilution by tributaries,
 123 and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

124 In community C (downstream of a PFAS manufacturing site), legacy PFAS concentrations were
 125 low, and only mean (and median) concentrations of PFBA and PFPeA were >QLs. However,
 126 high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA
 127 concentration (631 ng/L) was approximately eight times the average summed PFCA and PFSA
 128 concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis.
 129 Similar to communities A and B, the highest PFAS concentrations for community C were also
 130 observed at low flow (Figure S3 in SI).



131

132 Figure 1. PFAS occurrence at drinking water intakes in the CFR watershed. Concentrations
 133 represent averages of samples collected between June and December 2013. Individual samples

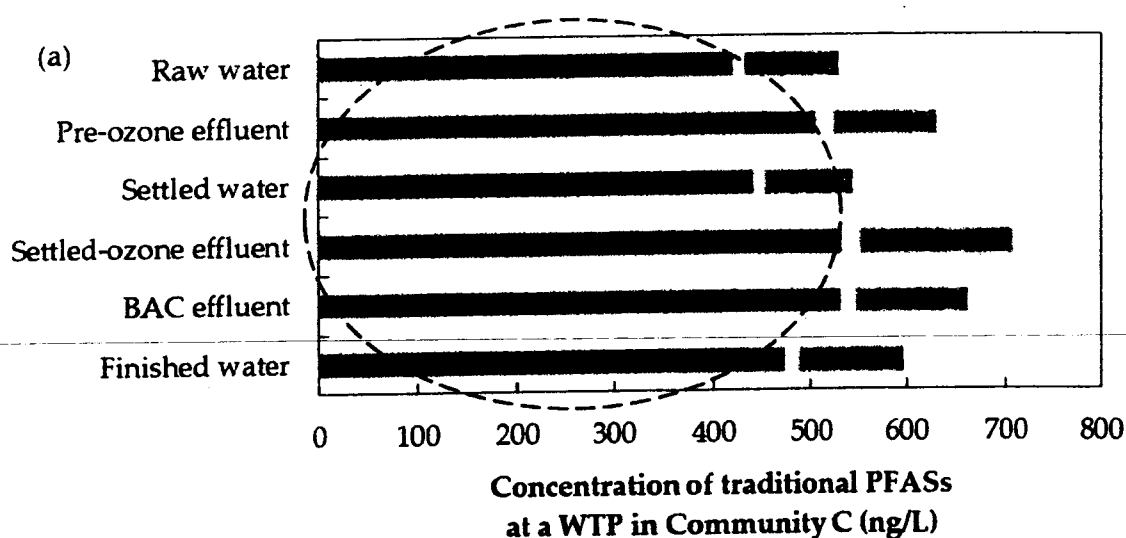
134 with concentrations < QLs were considered as 0 when calculating averages, and average
135 concentrations < QLs were not plotted.

136

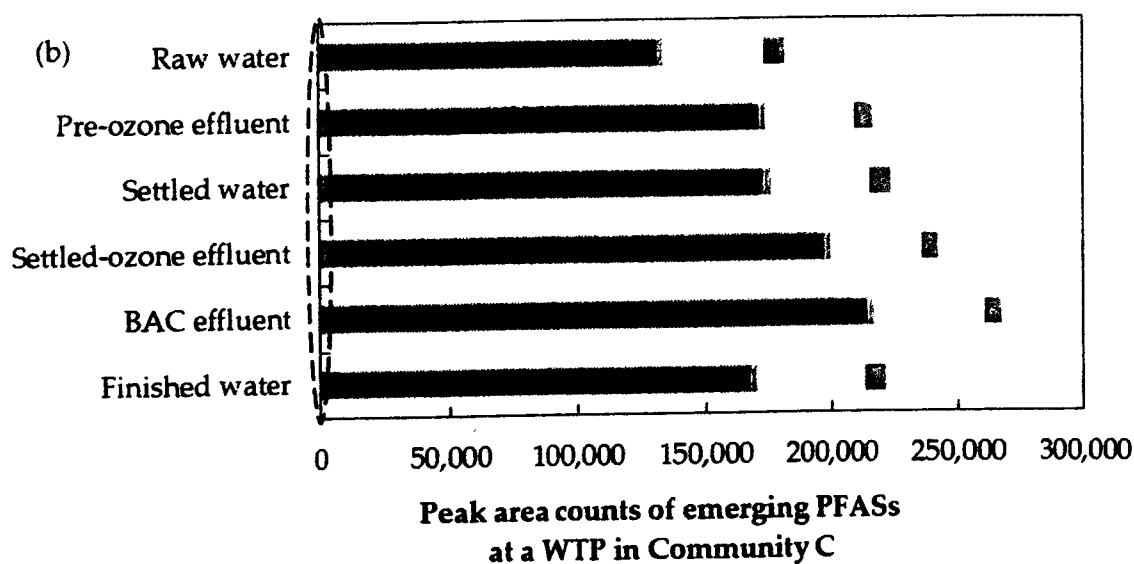
137 **PFAS fate in conventional and advanced water treatment processes:** To investigate whether
138 PFASs can be removed from the impacted source water, samples from DWTP C were collected
139 at the intake and after each treatment step. Results in Figure 2 suggest conventional and several
140 advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water
141 ozonation, BAC filtration, and disinfection by medium pressure UV lamps and free chlorine)
142 did not remove legacy PFASs, consistent with previous reports.²¹⁻²⁵ The data further illustrate
143 that no measurable PFECAs removal occurred in this DWTP. Concentrations of some PFCAs,
144 PFSA, PFMOPrA, PFPrOPrA and PFMOAA may have increased after ozonation, possibly due
145 to the oxidation of precursor compounds.²⁴ Disinfection with medium pressure UV lamps and
146 free chlorine (located between BAC effluent and the finished water) may have decreased
147 concentrations of PFMOAA, PFMOPrA, PFMOBA and PFPrOPrA, but only to a limited extent.

148 Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was
149 similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in
150 Figure 1; i.e., PFPrOPrA concentrations (400-500 µg/L) greatly exceeded legacy PFAS
151 concentrations. Moreover, three PFECAs (PFMOAA, PFO₂HxA and PFO₃OA)¹¹ had peak areas
152 2-113 times greater than that of PFPrOPrA (Figure 2b). The existence of high levels of emerging
153 PFASs suggests the necessity of incorporating them into routine monitoring.

154



■ PFPrOPrA PFBA ■ PFPeA ■ PFHxA ■ PFHpA ■ PFOA
 ■ PFNA ■ PFDA ■ PFBS ■ PFHS ■ PFOS



■ PFPrOPrA ■ PFMOAA ■ PFMOPrA ■ PFMOBA
 PFO2HxA ■ PFO3OA PFO4DA

Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for emerging PFECAs, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted in dashed ovals for reference. Compounds with concentrations <QL were not plotted.

162 **PFAS adsorption by PAC:** PAC can effectively remove long-chain PFCAs and PFSA, but its
163 effectiveness decreases with decreasing PFAS chain length.^{23, 24, 28} It is unclear, however, how the
164 presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 hour, a
165 PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with carbon chain length ≥ 7 . At
166 a PAC dose of 60 mg/L, >80% removal was achieved for PFCAs with carbon chain length ≥ 8
167 over the same time. At a PAC dose of 100 mg/L, removals were 95% for PFO₄DA and 54% for
168 PFO₃OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC
169 contact time are shown in Figure S5 in SI. PFMOAA could not be quantified by the analytical
170 method used in this test; however, based on the observations that PFAS adsorption decreases
171 with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than
172 PFMOAA (i.e., PFMOPrA and PFMOBA) were poorly adsorbed by PAC (Figure 3), it is
173 expected that PFMOAA adsorption is negligible at the tested conditions.

174 To compare the affinity of different PFASs for PAC, the PFAS removal percentages in solution
175 were plotted as a function of PFAS chain length (the sum of carbon (including branched), ether
176 oxygen, and sulfur atoms) (Figure 3(b)). The adsorbability of both legacy and emerging PFASs
177 increased with increasing chain length. PFSA were more readily removed than PFCAs of
178 matching chain length, which agrees with previous studies.^{23, 24, 28} PFECAs exhibited lower
179 adsorbabilities than PFCAs of the same chain length (e.g. PFMOBA < PFHxA), suggesting that
180 the replacement of a CF₂ group with an ether oxygen atom decreases the affinity of PFASs for
181 PAC. However, the replacement of additional CF₂ groups with ether groups resulted in small or
182 negligible affinity changes among the studied PFECAs (e.g., PFMOBA ~ PFO₂HxA).
183 Alternatively, if only the number of perfluorinated carbons were considered as a basis of
184 comparing adsorbability, the interpretation would be different. In that case, with the same
185 number of perfluorinated carbons, PFCAs have a higher affinity for PAC than mono-ether
186 PFECAs (e.g., PFPeA > PFMOBA), but a lower affinity than multi-ether PFECAs (e.g.,
187 PFPeA < PFO₃OA).

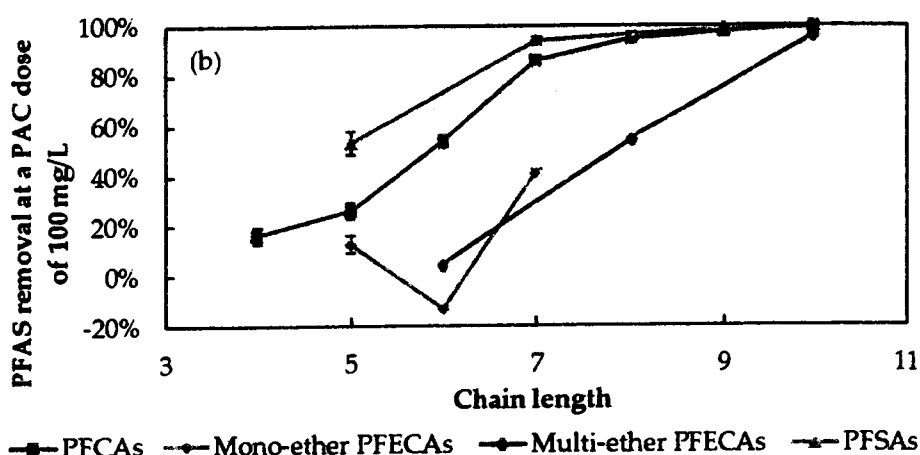
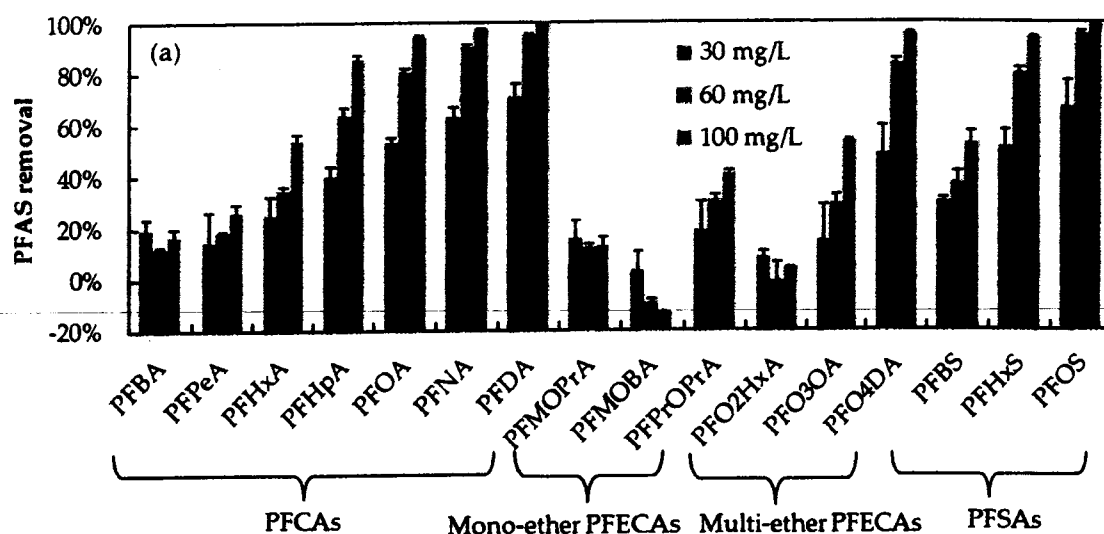


Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60 and 100 mg/L and (b) as a function of PFAS chain length. PAC contact time in CFR water was 1 hour. Legacy PFASs were spiked at ~1000 ng/L and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

In either framework, it is clear that the presence of ether groups in PFECAs changes their propensity to leave the aqueous phase and adsorb on PAC. It can thus be inferred that the incorporation of ether groups changes physiochemical properties, such as the octanol-water

199 partition coefficient and aqueous solubility of PFECAs relative to PFCAs. Consequently, it is
200 reasonable to expect that fate and transport of PFECAs in natural and engineered systems will
201 differ from that of legacy PFCAs. For example, while PFPrOPrA ("GenX") may be less
202 bioaccumulative than PFOA, which it is replacing, the adsorption data here suggest PFPrOPrA
203 is less hydrophobic than PFOA. Thus, when released to the environment, PFPrOPrA has a
204 higher tendency to remain in the aqueous phase and is more difficult to remove from drinking
205 water sources by adsorptive means.

206 To the knowledge of the authors, this is the first paper reporting the behavior of recently
207 identified PFECAs in water treatment processes. This work documents concentrations of legacy
208 PFASs over the course the CFR, and the emergence of PFECAs as an important class of
209 fluorinated alternatives that dominated the PFAS signature downstream of a PFAS
210 manufacturer. The relatively low concentrations of legacy PFASs in the finished drinking water
211 of community C are consistent with data reported from this DWTP in the third unregulated
212 contaminant monitoring rule (UCMR3) conducted by USEPA³¹. However, the detection of
213 potentially high levels of PFECAs, and the difficulty to effectively remove not only legacy
214 PFASs but also PFECAs with many water treatment processes, suggest the need for broader
215 discharge control and contaminant monitoring.

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219 views expressed in this article are those of the authors and do not necessarily represent the
220 views or policies of the USEPA.

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Legacy and emerging perfluoroalkyl substances in the Cape Fear River Watershed of North Carolina: Occurrence and fate during conventional and advanced water treatment processes

Mei Sun^{1,2,*}, Elisa Arevalo², Mark Strynar³, Andrew Lindstrom³, and Detlef R.U. Knappe²

Supporting information includes analytical method description, 6 tables, and 5 figures.

¹Department of Civil and Environmental Engineering

University of North Carolina at Charlotte

Charlotte, North Carolina 28223, USA

²Department of Civil, Construction, and Environmental Engineering,

North Carolina State University, Campus Box 7908

Raleigh, North Carolina 28695, USA

³National Exposure Research Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, North Carolina 27711, USA

Analytical standards: PFASs studied in this research are listed in Table S1. For legacy PFASs, native and isotopically labeled standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Native PFPrOPrA was purchased from Thermo Fisher Scientific (Waltham, MA). No analytical standards were available for other PFECAs.

PFAS quantification: PFAS concentrations in samples from DWTPs and adsorption tests were determined by liquid chromatography tandem mass spectrometry (LC-MS/MS) using a large-volume (0.9 mL) direct injection method. An Agilent 1100 Series LC pump and PE Sciex API 3000 LC-MS/MS system equipped with a 4.6 mm x 50 mm HPLC column (Kinetex C18 5 μ m 100Å, Phenomenex Inc.) was used for PFAS analysis. The eluent gradient is shown in Table S4 in SI. All samples, calibration standards, and quality control samples were spiked with isotopically labeled internal standards, filtered through 0.45- μ m glass microfiber syringe filters, and analyzed in duplicate. The MS transitions for PFAS analytes and internal standards are shown in Table S5 in SI. The quantitation limit (QL) was 25 ng/L for PFOS and perfluorodecanoic acid, and 10 ng/L for other legacy PFASs and PFPrOPrA. For PFECAs without analytical standards, chromatographic peak areas are reported.

PFAS concentrations along the treatment train of DWTP C were analyzed using a Waters Acquity ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (Waters, Milford, MA, USA) after solid phase extraction. Method details are described elsewhere.¹ The QL for all PFASs with analytical standards was 0.2 ng/L, and peak areas were recorded for PFECAs without standards.

Table S1. Perfluoroalkyl substances (PFASs) detected in the Cape Fear River (CFR) watershed

Compound	Molecular weight	Formula	CAS	# of perfluorinated carbons	Chain length (including all C, O and S)
Perfluorocarboxylic acids (PFCAs)					
Perfluorobutanoic acid (PFBA)	214.0	C ₄ HF ₉ O ₂	375-22-4	3	4
Perfluoropentanoic acid (PFPeA)	264.0	C ₅ HF ₉ O ₂	2706-90-3	4	5
Perfluorohexanoic acid (PFHxA)	314.1	C ₆ HF ₁₁ O ₂	307-24-4	5	6
Perfluoroheptanoic acid (PFHpA)	364.1	C ₇ HF ₁₃ O ₂	375-85-9	6	7
Perfluorooctanoic acid (PFOA)	414.1	C ₈ HF ₁₅ O ₂	335-67-1	7	8
Perfluorononanoic acid (PFNA)	464.1	C ₉ HF ₁₇ O ₂	375-95-1	8	9
Perfluorodecanoic acid (PFDA)	514.1	C ₁₀ HF ₁₉ O ₂	335-76-2	9	10
Perfluorosulfonic acids (PFSAAs)					
Perfluorobutane sulfonic acid (PFBS)	300.1	C ₄ HF ₉ SO ₃	29420-49-3	4	5
Perfluorohexane sulfonic acid (PFHxS)	438.2	C ₆ HF ₁₃ SO ₃	355-46-4	6	7
Perfluorooctane sulfonic acid (PFOS)	500.1	C ₈ HF ₁₇ SO ₃	111873-33-7	8	9
Perfluoroalkyl ether carboxylic acids with one ether group (mono-ether PFECAs)					
Perfluoro-2-methoxyacetic acid (PFMOAA)	180.0	C ₃ HF ₅ O ₃	674-13-5	2	4
Perfluoro-3-methoxypropanoic acid (PFMOPrA)	230.0	C ₄ HF ₇ O ₃	377-73-1	3	5
Perfluoro-4-methoxybutanoic acid (PFMOBA)	280.0	C ₅ HF ₉ O ₃	863090-89-5	4	6
Perfluoro-2-propoxypropanoic acid (PFPPrOPrA)	330.1	C ₆ HF ₁₁ O ₃	13252-13-6	5	7
Perfluoroalkyl ether carboxylic acids with multiple ether group (multi-ether PFECAs)					
Perfluoro(3,5-dioxahexanoic) acid (PFO2HxA)	246.0	C ₄ HF ₇ O ₄	39492-88-1	3	6
Perfluoro(3,5,7-trioxaoctanoic) acid (PFO3OA)	312.0	C ₅ HF ₉ O ₅	39492-89-2	4	8
Perfluoro(3,5,7,9-tetraoxadecanoic) acid (PFO4DA)	378.1	C ₆ HF ₁₁ O ₆	39492-90-5	5	10

Table S2. Operational conditions of DWTP C on sampling day (August 18, 2014)

Parameter	Value
Raw water ozone dose	3.1 mg/L
Raw water total organic carbon concentration	6.0 mg/L
Aluminum sulfate coagulant dose	43 mg/L
Coagulation pH	5.70
Settled water ozone dose	1.3 mg/L
Settled water total organic carbon concentration	1.90 mg/L
Empty bed contact time in biological activated carbon filters	9.4 minutes for granular activated carbon layer 2.3 minutes for sand layer
Medium pressure UV dose	25 mJ/cm ²
Free chlorine dose	1.26 mg/L as Cl ₂
Free chlorine contact time	17.2 hours

Table S3. Water quality characteristics of surface water used in adsorption tests

Non-purgeable organic carbon (mg/L)	Ultraviolet absorbance at a wavelength of 254 nm	pH	Alkalinity (mg/L as CaCO ₃)	Conductivity (µS/cm)
9.036	0.399	7.53	19	133.5

Table S4. LC gradient method for PFAS analysis

Time (min)	Mobile Phase A% (v/v)	Mobile Phase B%	Flow Rate (mL/min)
0 – 2	95	5	0.9
2 – 5	95	5	0.9
5 – 10	95 → 10	5 → 90	0.9
10 – 10.1	10	90	0.9
10.1 – 14	10 → 95	90 → 5	0.9

Mobile phase A: 2 mM ammonium acetate in ultrapure water with 5% methanol

Mobile phase B: 2 mM ammonium acetate in acetonitrile with 5% ultrapure water

Table S5. MS transitions for PFAS Analysis

Compound		MS/MS Transition	Internal standard
Legacy PFASs	PFBA	212.8 → 168.8	13C4-PFBA
	PFPeA	262.9 → 218.8	13C2- PFHxA
	PFHxA	313.6 → 268.8	13C2- PFHxA
	PFHpA	362.9 → 318.8	13C4- PFOA
	PFOA	413.0 → 368.8	13C4- PFOA
	PFNA	463.0 → 418.8	13C4- PFOA
	PFDA	513.1 → 68.8	13C2-PFDA
	PFBS	299.1 → 98.8	18O2-PFHxS
	PFHxS	399.1 → 98.8	18O2-PFHxS
	PFOS	498.9 → 98.8	13C4-PFOS
PFECAs	PFMOAA	180.0 → 85.0	N/A
	PFMOPrA	229.1 → 184.9	N/A
	PFMOBA	279.0 → 234.8	N/A
	PFPPrOPrA	329.0 → 284.7	13C2- PFHxA
	PFO2HxA	245.1 → 85.0	N/A
	PFO3OA	311. → 84.9	N/A
	PFO4DA	377.1 → 85.0	N/A
Internal standards	Perfluoro-n-[1,2,3,4- ¹³ C ₄]butanoic acid (13C4-PFBA)	217.0 → 172	Not applicable
	Perfluoro-n-[1,2- ¹³ C ₂]hexanoic acid (13C2-PFHxA)	315.1 → 269.8	
	Perfluoro-n-[1,2,3,4- ¹³ C ₂]octanoic acid (13C4-PFOA)	417.0 → 372.0	
	Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid (13C2-PFDA)	515.1 → 469.8	
	Sodium perfluoro-1-hexane[¹⁸ O ₂]sulfonate (18O2-PFHxS)	403.1 → 83.8	
	Sodium perfluoro-1-[1,2,3,4- ¹³ C ₄]octane sulfonate (13C4-PFOS)	502.9 → 79.9	

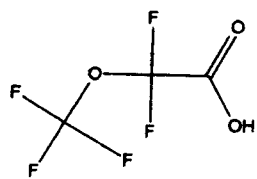
Table S6. Maximum, minimum, mean and median concentrations (ng/L) of PFASs in CFR watershed surface water as drinking water sources. *

	Community A				Community B				Community C			
	max	min	median	mean	max	min	median	mean	max	min	median	mean
PFBA	99	<10	26	33	38	<10	12	12	104	<10	12	22
PFPeA	191	14	44	62	38	<10	19	19	116	<10	30	36
PFHxA	318	<10	48	78	42	<10	<10	11	24	<10	<10	<10
PFHpA	324	<10	39	67	85	<10	<10	11	24	<10	<10	<10
PFOA	137	<10	34	46	32	<10	<10	<10	17	<10	<10	<10
PFNA	38	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
PFDA	35	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
PFBS	80	<10	<10	<10	11	<10	<10	<10	<10	<10	<10	<10
PFHxS	193	<10	10	14	14	<10	<10	<10	14	<10	<10	<10
PFOS	346	<25	29	44	43	<25	<25	<25	40	<25	<25	<25
PFPrOPrA	<10	<10	<10	<10	10	<10	<10	<10	4560	55	304	631
PFOA+PFOS	447	0	64	90	59	0	0	9	55	<10	<10	<10
Σ PFASs**	1502	18	212	355	189	0	47	62	4696	55	345	710

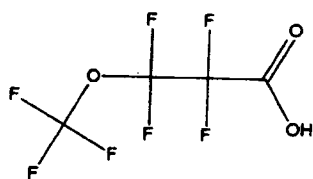
* Concentrations < quantification limits were considered as zero to calculate means and Σ PFASs.

** Other PFECAs were present in water samples from community C but could not be quantified and were therefore not included in Σ PFASs

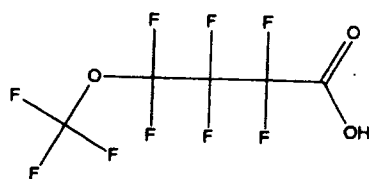
Figure S1. Molecular structures of PEFCAs in this study



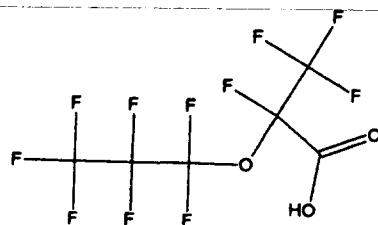
PFMOAA



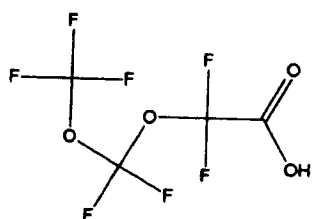
PFMOPrA



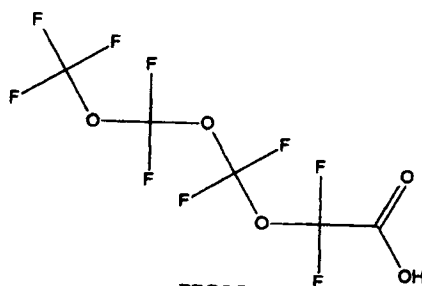
PFMOBA



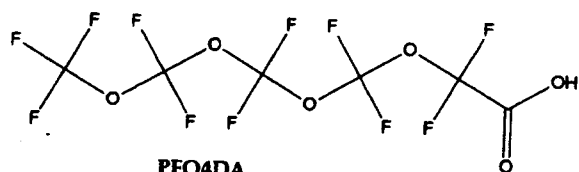
PFPrOPrA



PFO2HxA



PFO3OA



PFO4DA

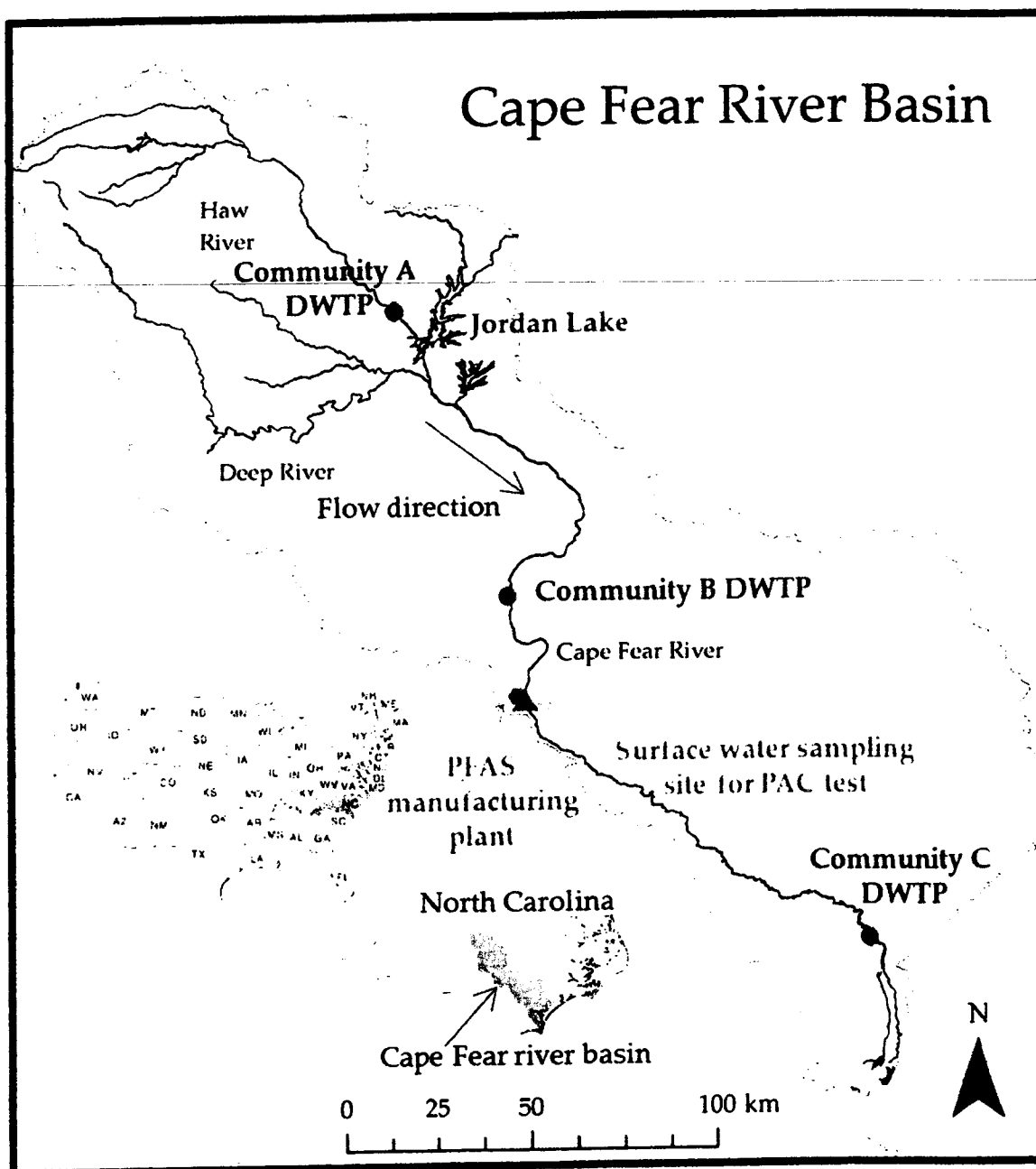
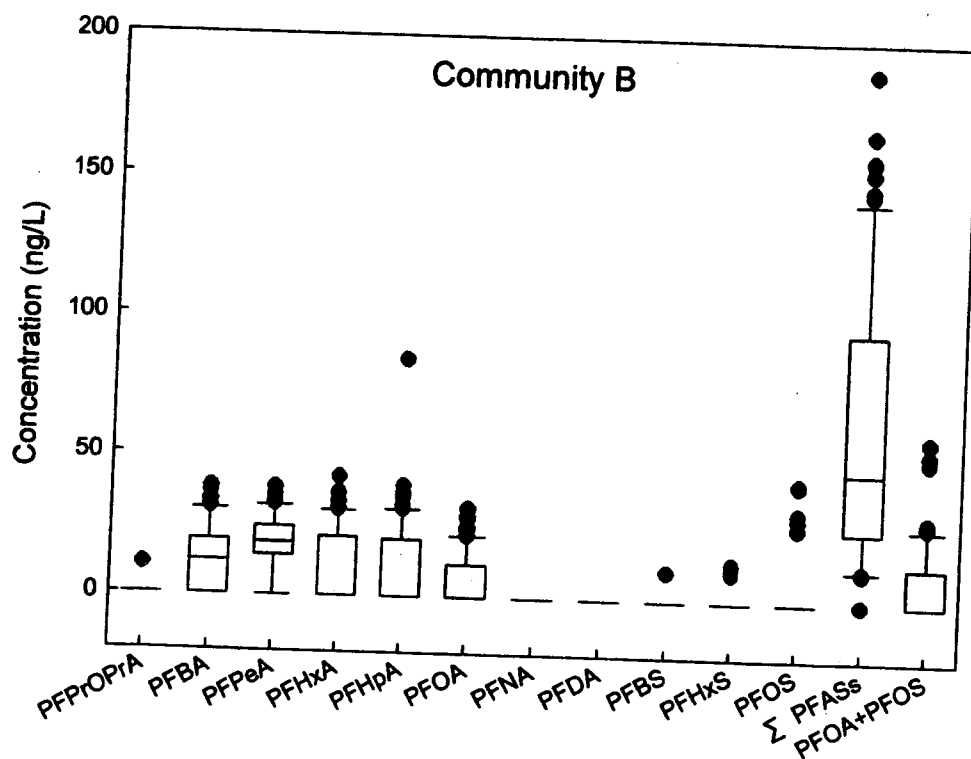
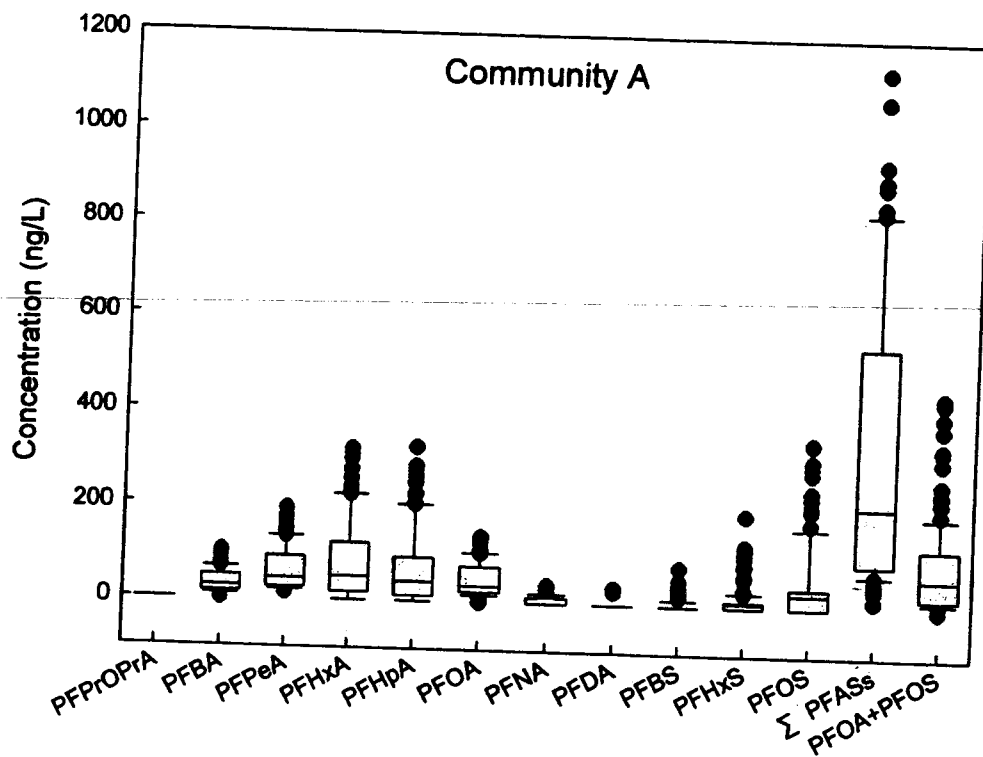


Figure S2. Sampling sites in the Cape Fear River watershed, North Carolina



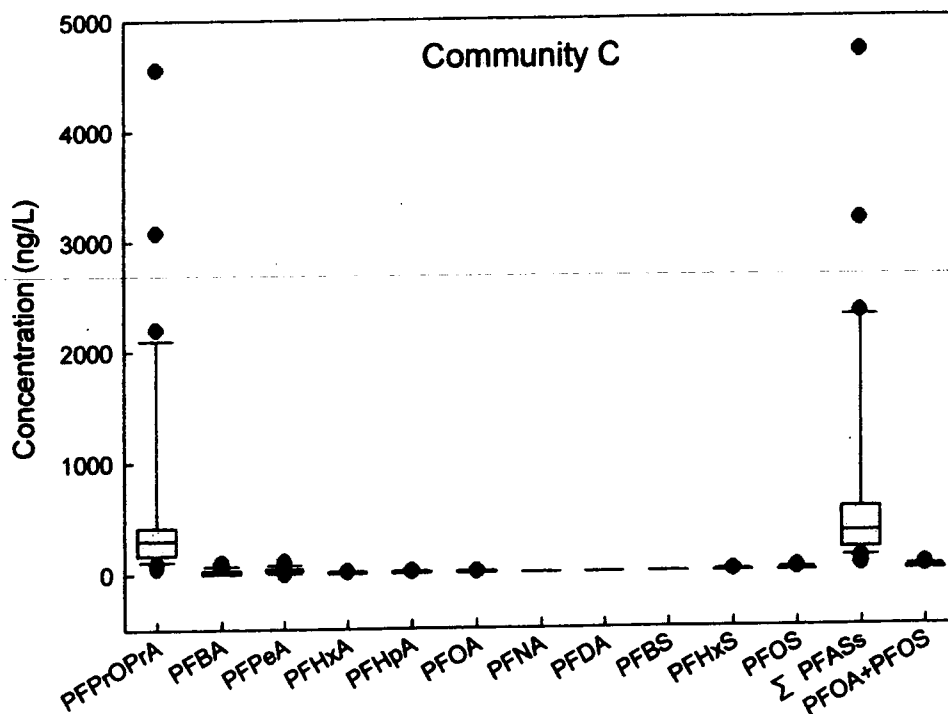


Figure S3. PFAS concentration distributions in the CFR watershed at three drinking water intakes. Concentrations < quantification limits were considered as zero. The upper and lower edges of a box represent the 75th and 25th percentile, respectively; the middle line represents the median; the upper and lower bars represent the 90th and 10th percentile, respectively; the dots represent outliers (>90th or <10th percentile).

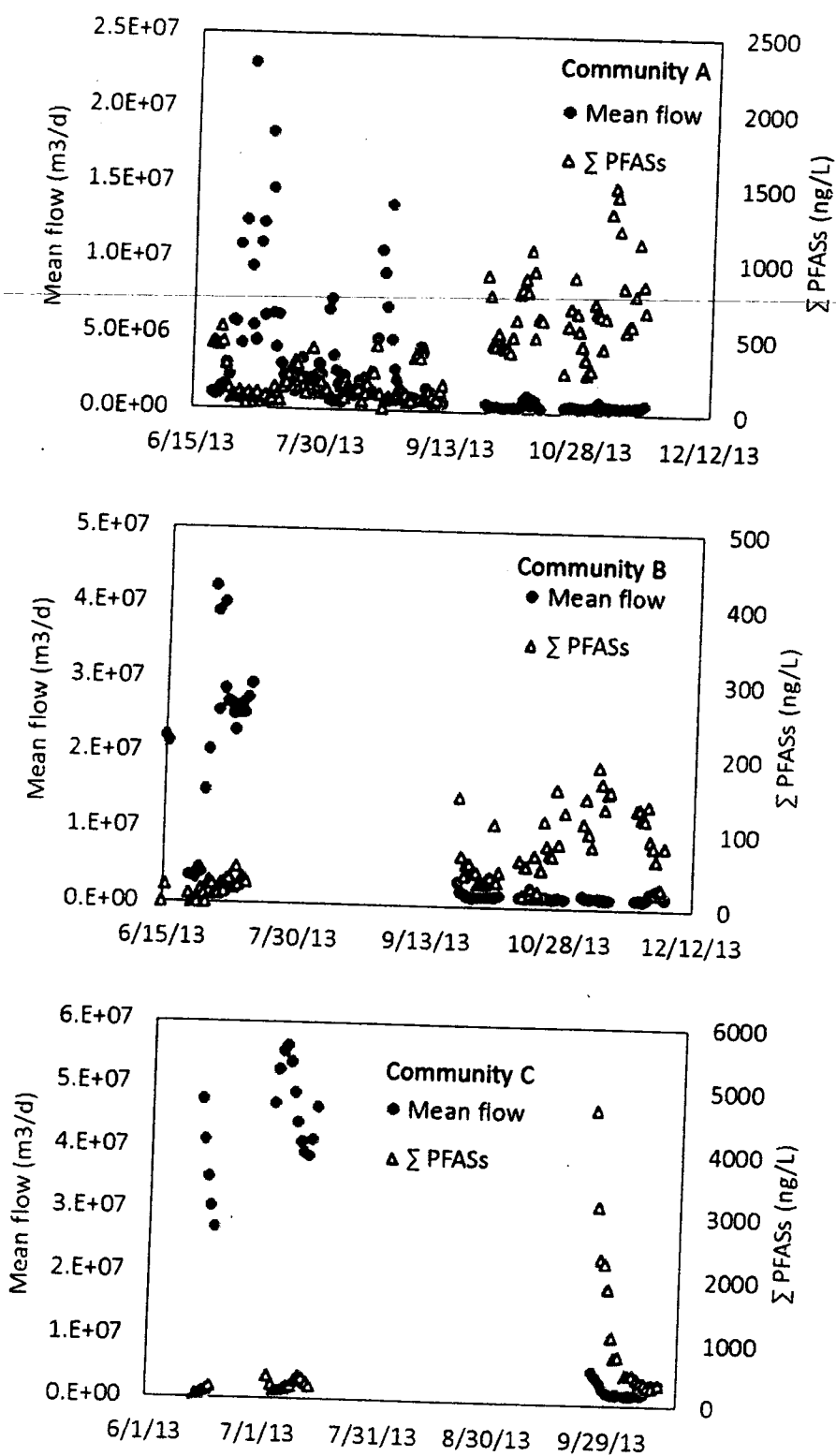


Figure S4. Total PFAS concentrations in the source water and stream flow at the three studied DWTPs. Stream flow data were acquired from US Geological Survey stream gage records

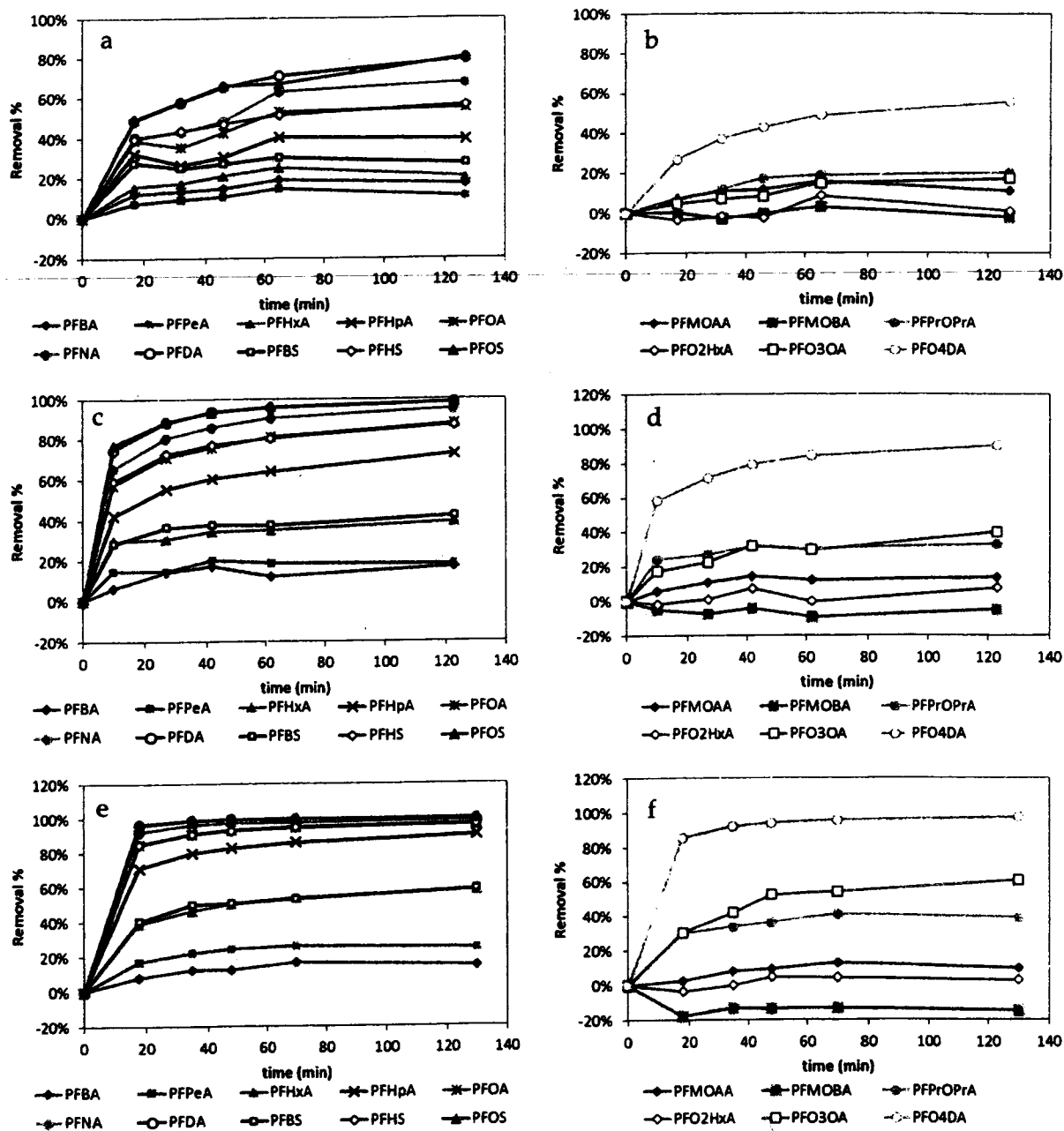


Figure S5. PFAS adsorption on PAC at carbon doses of (a, b) 30 mg/L, (c, d) 60 mg/L and (e, f) 100 mg/L. Figures show average PFAS removal percentages of duplicate tests.

Reference

1. Nakayama, S.; Strynar, M. J.; Helfant, L.; Egeghy, P.; Ye, X.; Lindstrom, A. B., Perfluorinated compounds in the Cape Fear drainage basin in North Carolina. *Environmental Science & Technology* 2007, 41, (15), 5271-5276.

John Malone

From: Detlef Knappe <knappe@ncsu.edu>
Sent: Sunday, September 25, 2016 10:31 PM
To: Ben Kearns
Cc: Michael Richardson
Subject: Re: Paper draft

Excellent! We will add you.

Detlef

On 9/25/16 10:50 AM, Ben Kearns wrote:

> Hey Detlef,

>

> I apologize for the late response. This week has been interesting with Mike packing up and his retirement festivities.

> Yes, we would be grateful if you added us as co-authors. I do not have any comments on it at this time.

>

> Regards,

>

> Ben Kearns

>

> Sent from my iPhone

>

>> On Sep 24, 2016, at 8:03 PM, Detlef Knappe <knappe@ncsu.edu> wrote:

>>

>> Hi Ben and Mike,

>>

>> I hope you are having a good weekend. Do you have any comments and interest in co-authorship on the PFAS paper I sent you?

>>

>> Best,

>>

>> Detlef

>>

>>

>> --

>> Detlef Knappe

>> Professor

>> 319-E Mann Hall

>> Department of Civil, Construction, and Environmental Engineering

>> North Carolina State University Campus Box 7908 Raleigh, NC

>> 27695-7908

>>

>> Phone: 919-515-8791

>> Fax: 919-515-7908

>> E-mail: knappe@ncsu.edu

>> Web page: <http://knappelab.wordpress.ncsu.edu/>

>>

--

Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Beth Eckert

From: Mallin, Michael A. <mallinm@uncw.edu>
Sent: Tuesday, November 29, 2016 3:58 PM
To: Polera, Madison Elise; Beth Eckert; Cahoon, Larry; chad.ham@faypwc.com; Deaton, Anne; diana_rashash@ncsu.edu; Fitz Rhode; kemp@cfrw.us; kristina.fischer@ncagr.gov; Mike Giles; Mike_Wicker@fws.gov; nora.deamer@ncdenr.gov; pam.ellis@cfpua.org; janine.harris@noaa.gov; Jennifer Alford; slharden@usgs.gov; Saul, Bradley; Vander Borgh, Mark; Prescott, James Carlyle
Cc: dyork@dialcordy.com; cmpolera@outlook.com
Subject: recent Cape Fear River paper
Attachments: Sun_etal_ESTL_2016.pdf

Folks – recent CFR paper from NCSU,
Mike

Dr. Michael A. Mallin
Research Professor
Center for Marine Science
University of North Carolina Wilmington
Wilmington, N.C. 28409
Phone: 910 962-2358
Fax: 910 962-2410
Email: mallinm@uncw.edu
Lab website: <http://uncw.edu/cms/aelab/>

*published
paper
attached*

Beth Eckert

From: Ben Kearns
Sent: Tuesday, March 7, 2017 2:34 PM
To: Beth Eckert
Subject: FW: New PEAS paper
Attachments: NeverEndingStory_EST2017.pdf

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, March 06, 2017 6:01 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: New PFAS paper

Hi Ben,

I enjoyed our conversation. This paper gives a good overview of the overall challenge associated with PFAS releases into the environment.

Best,

Detlef

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

Beth Eckert

From: Ben Kearns
Sent: Tuesday, March 7, 2017 2:34 PM
To: Beth Eckert
Subject: FW: Paper
Attachments: PFECAs_Sun_ESTL2016.pdf; PFECAs_Sun_ESTL2016_SI.pdf

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, March 06, 2017 4:16 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Paper

--

Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

Beth Eckert

From: Jill Deaney
Sent: Thursday, June 15, 2017 3:08 PM
To: Beth Eckert
Subject: FW: Paper
Attachments: PFECAs_Sun_ESTL2016.pdf; PFECAs_Sun_ESTL2016_SI.pdf

-----Original Message-----

From: Ben Kearns
Sent: Tuesday, March 07, 2017 1:52 PM
To: Jill Deaney <Jill.Deaney@cfpua.org>; Allyson Ridout <Allyson.Ridout@cfpua.org>
Subject: FW: Paper

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, March 06, 2017 4:16 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Paper

--
Detlef Knappe
Professor
319-E Mann Hall
Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791
Fax: 919-515-7908
E-mail: knappe@ncsu.edu
Web page: <http://knappelab.wordpress.ncsu.edu/>

Beth Eckert

From: Jill Deaney
Sent: Thursday, June 15, 2017 3:08 PM
To: Beth Eckert
Subject: FW: Emerging PFASs to add to the list to monitor

From: Ben Kearns
Sent: Tuesday, March 07, 2017 2:52 PM
To: Allyson Ridout <Allyson.Ridout@cfpua.org>; Jill Deaney <Jill.Deaney@cfpua.org>
Subject: Emerging PFASs to add to the list to monitor

Hey Jill and Allyson,

In reading further down the paper the following emerging (new replacement) compounds would also be good to investigate whether a lab can run them. They were the main compounds found in Community C unit processes.

- PFMOAA – perfluoro-2-methoxyacetic acid
- PFO2HxA – perfluoro-(3,5-dioxahexanoic) acid
- PFO3OA – perfluoro (3,5,7-trioxaoctanoic) acid
- PFPrOPrA – perfluoro-2-propoxypropanoic acid

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina

Mei Sun,^{*,†,‡} Elisa Arevalo,[‡] Mark Strynar,[§] Andrew Lindstrom,[§] Michael Richardson,^{||} Ben Kearns,^{||} Adam Pickett,[⊥] Chris Smith,[#] and Detlef R. U. Knappe[‡]

[†]Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, United States

[‡]Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[§]National Exposure Research Laboratory, U.S. Environmental Protection Agency Research, Triangle Park, North Carolina 27711, United States

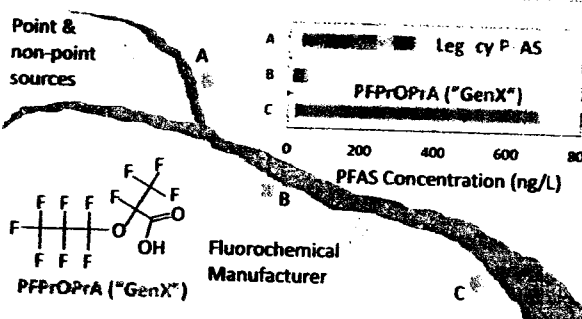
^{||}Cape Fear Public Utility Authority, Wilmington, North Carolina 28403, United States

[⊥]Town of Pittsboro, Pittsboro, North Carolina 27312, United States

[#]Fayetteville Public Works Commission, Fayetteville, North Carolina 28301, United States

Supporting Information

ABSTRACT: Long-chain per- and polyfluoroalkyl substances (PFASs) are being replaced by short-chain PFASs and fluorinated alternatives. For ten legacy PFASs and seven recently discovered perfluoroalkyl ether carboxylic acids (PFECAs), we report (1) their occurrence in the Cape Fear River (CFR) watershed, (2) their fate in water treatment processes, and (3) their adsorbability on powdered activated carbon (PAC). In the headwater region of the CFR basin, PFECAs were not detected in raw water of a drinking water treatment plant (DWTP), but concentrations of legacy PFASs were high. The U.S. Environmental Protection Agency's lifetime health advisory level (70 ng/L) for perfluorooctanesulfonic acid and perfluorooctanoic acid (PFOA) was exceeded on 57 of 127 sampling days. In raw water of a DWTP downstream of a PFAS manufacturer, the mean concentration of perfluoro-2-propoxypropanoic acid (PFPrOPrA), a replacement for PFOA, was 631 ng/L ($n = 37$). Six other PFECAs were detected, with three exhibiting chromatographic peak areas up to 15 times that of PFPrOPrA. At this DWTP, PFECA removal by coagulation, ozonation, biofiltration, and disinfection was negligible. The adsorbability of PFASs on PAC increased with increasing chain length. Replacing one CF_2 group with an ether oxygen decreased the affinity of PFASs for PAC, while replacing additional CF_2 groups did not lead to further affinity changes.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are extensively used in the production of plastics, water/stain repellents, firefighting foams, and food-contact paper coatings. The widespread occurrence of PFASs in drinking water sources is closely related to the presence of sources such as industrial sites, military fire training areas, civilian airports, and wastewater treatment plants.¹ Until 2000, long-chain perfluoroalkyl sulfonic acids [$\text{C}_n\text{F}_{2n+1}\text{SO}_3\text{H}$; $n \geq 6$ (PFASs)] and perfluoroalkyl carboxylic acids [$\text{C}_n\text{F}_{2n+1}\text{COOH}$; $n \geq 7$ (PFCAs)] were predominantly used.² Accumulating evidence about the ecological persistence and human health effects associated with exposure to long-chain PFASs^{3,4} has led to an increased level of regulatory attention. Recently, the U.S. Environmental Protection Agency (USEPA) established a lifetime health

advisory level (HAL) of 70 ng/L for the sum of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) concentrations in drinking water.^{5,6} Over the past decade, production of long-chain PFASs has declined in Europe and North America, and manufacturers are moving toward short-chain PFASs and fluorinated alternatives.^{7–10} Some fluorinated alternatives were recently identified,^{8,11} but others remain unknown^{12–14} because they are either proprietary or manufacturing byproducts.

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Accepted: November 10, 2016

Published: November 10, 2016

One group of fluorinated alternatives, perfluoroalkyl ether carboxylic acids (PFECAs), was recently discovered in the Cape Fear River (CFR) downstream of a PFAS manufacturing facility.¹¹ Identified PFECAs included perfluoro-2-methoxyacetic acid (PFMOAA), perfluoro-3-methoxypropanoic acid (PFMOPrA), perfluoro-4-methoxybutanoic acid (PFMOBA), perfluoro-2-propoxypropanoic acid (PFPrOPrA), perfluoro-(3,5-dioxahexanoic) acid (PFO2HxA), perfluoro-(3,5,7-trioxaoctanoic) acid (PFO3OA), and perfluoro-(3,5,7,9-tetraoxadecanoic) acid (PFO4DA) (Table S1 and Figure S1). The ammonium salt of PFPrOPrA is a known PFOA alternative¹⁵ that has been produced since 2010 with the trade name “GenX”. To the best of our knowledge, the only other published PFECA occurrence data are for PFPrOPrA in Europe and China,¹⁵ and no published data about the fate of PFECAs during water treatment are available. Except for a few studies (most by the manufacturer),^{16–20} little is known about the toxicity, pharmacokinetic behavior, or environmental fate and transport of PFECAs.

The strong C–F bond makes PFASs refractory to abiotic and biotic degradation,²¹ and most water treatment processes are ineffective for legacy PFAS removal.^{22–27} Processes capable of removing PFCAs and PFASs include nanofiltration,²⁸ reverse osmosis,²⁵ ion exchange,^{28,29} and activated carbon adsorption,^{28,29} with activated carbon adsorption being the most widely employed treatment option.

The objectives of this research were (1) to identify and quantify the presence of legacy PFASs and emerging PFECAs in drinking water sources, (2) to assess PFAS removal by conventional and advanced processes in a full-scale drinking water treatment plant (DWTP), and (3) to evaluate the adsorbability of PFASs on powdered activated carbon (PAC).

MATERIALS AND METHODS

Water Samples. Source water of three DWTPs treating surface water in the CFR watershed was sampled between June 14 and December 2, 2013 (Figure S2). Samples were collected from the raw water tap at each DWTP daily as either 8 h composites (DWTP A, 127 samples) or 24 h composites (DWTP B, 73 samples; DWTP C, 34 samples). Samples were collected in 250 mL HDPE bottles and picked up (DWTPs A and B) or shipped overnight (DWTP C) on a weekly basis. All samples were stored at room temperature until they were analyzed (within 1 week of receipt). PFAS losses during storage were negligible on the basis of results of a 70 day holding study at room temperature. On August 18, 2014, grab samples were collected at DWTP C after each unit process in the treatment train [raw water ozonation, coagulation/flocculation/sedimentation, settled water ozonation, biological activated carbon (BAC) filtration, and disinfection by medium-pressure UV lamps and free chlorine]. Operational conditions of DWTP C on the sampling day are listed in Table S2. Samples were collected in 1 L HDPE bottles and stored at room temperature until they were analyzed. On the same day, grab samples of CFR water were collected in six 20 L HDPE carboys at William O. Huske Lock and Dam downstream of a PFAS manufacturing site and stored at 4 °C until use in PAC adsorption experiments (background water matrix characteristics listed in Table S3).

Adsorption Experiments. Adsorption of PFASs by PAC was studied in batch reactors (amber glass bottles, 0.45 L of CFR water). PFECA adsorption was studied at ambient concentrations (~1000 ng/L PFPrOPrA, chromatographic peak areas of other PFECAs being approximately 10–800%

of the PFPrOPrA area). Legacy PFASs were present at low concentrations (<40 ng/L) and spiked into CFR water at ~1000 ng/L each. Data from spiked and nonspiked experiments showed that the added legacy PFASs and methanol (1 ppm) from the primary stock solution did not affect native PFECA removal. A thermally activated, wood-based PAC (PicaHydro MP23, PICA USA, Columbus, OH; mean diameter of 12 μ m, BET surface area of 1460 m²/g)³⁰ proven to be effective for PFAS removal in a prior study²⁹ was used at doses of 30, 60, and 100 mg/L. These doses represent the upper feasible end for drinking water treatment. Samples were taken prior to and periodically after PAC addition for PFAS analysis. PFAS losses in PAC-free blanks were negligible.

PFAS Analysis. Information about analytical standards and liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods for PFAS quantification is provided in the Supporting Information.

RESULTS AND DISCUSSION

Occurrence of PFASs in Drinking Water Sources. Mean PFAS concentrations in source water of three DWTPs treating surface water from the CFR watershed are shown in Figure 1.

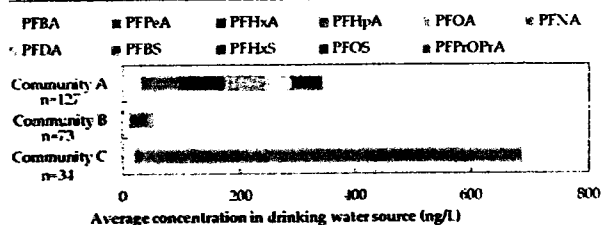


Figure 1. Occurrence of PFASs at drinking water intakes in the CFR watershed. Concentrations represent averages of samples collected between June and December 2013. Individual samples with concentrations below the quantitation limits (QLs) were considered as 0 when calculating averages, and average concentrations below the QLs were not plotted.

In communities A and B, only legacy PFASs were detected (mean Σ PFAS of 355 ng/L in community A and 62 ng/L in community B). Detailed concentration data are shown in Table S6 and Figure S3. In community A, PFCAs with four to eight total carbons, perfluorohexanesulfonic acid (PFHxS), and PFOS were detected at mean concentrations above the quantitation limits (QLs). During the 127 day sampling campaign, the sum concentration of PFOA and PFOS exceeded the USEPA HAL of 70 ng/L on 57 days. The mean sum concentration of PFOA and PFOS over the entire study period was 90 ng/L, with approximately equal contributions from PFOS (44 ng/L) and PFOA (46 ng/L). Maximum PFOS and PFOA concentrations were 346 and 137 ng/L, respectively. Similar PFOS and PFOA concentrations were observed in the same area in 2006,³¹ suggesting that PFAS source(s) upstream of community A have continued negative impacts on drinking water quality. Also, our data show that legacy PFASs remain as surface water contaminants of concern even though their production was recently phased out in the United States. It is important to note, however, that among the PFCAs that were measured in both 2006 and 2013 (PFHxA to PFDA), the PFCA speciation shifted from long-chain (~80–85% C_nF_{2n+1}COOH; $n = 7–9$) in 2006 to short-chain (76% C_nF_{2n+1}COOH; $n = 5–6$) in 2013. In contrast, the PFSA speciation was dominated by PFOS in both 2006 and 2013.

Relating total PFAS concentration to average daily streamflow (Figure S4) illustrated a general trend of low PFAS concentrations at high flow, and high concentrations at low flow, consistent with the hypothesis of one or more upstream point sources.

In community B, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA) were most frequently detected with mean concentrations of 12 and 19 ng/L, respectively. Mean PFOA and PFOS concentrations were below the QIs, and the maximum sum concentration of PFOA and PFOS was 59 ng/L. Lower PFAS concentrations in community B relative to community A can be explained by the absence of substantive PFAS sources between the two communities, dilution by tributaries, and the buffering effect of Jordan Lake, a large reservoir located between communities A and B.

In community C (downstream of a PFAS manufacturing site), only mean concentrations of PFBA and PFPeA were above the QIs. The relatively low concentrations of legacy PFASs in the finished drinking water of community C are consistent with results from the USEPA's third unregulated contaminant monitoring rule for this DWTP.³² However, high concentrations of PFPrOPrA were detected (up to ~4500 ng/L). The average PFPrOPrA concentration (631 ng/L) was approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L). Other PFECAs had not yet been identified at the time of analysis. Similar to communities A and B, the highest PFAS concentrations for community C were also observed at low flow (Figure S4). Stream flow data were used in conjunction with PFPrOPrA concentration data to determine PFPrOPrA mass fluxes at the intake of DWTP C. Daily PFPrOPrA mass fluxes ranged from 0.6 to 24 kg/day with a mean of 5.9 kg/day.

Fate of PFASs in Conventional and Advanced Water Treatment Processes. To investigate whether PFASs can be removed from impacted source water, samples from DWTP C were collected at the intake and after each treatment step. Results in Figure 2 suggest conventional and advanced treatment processes (coagulation/flocculation/sedimentation, raw and settled water ozonation, BAC filtration, and disinfection by medium-pressure UV lamps and free chlorine) did not remove legacy PFASs, consistent with previous studies.^{22–26} The data further illustrate that no measurable PFECAs were removed in this DWTP. Concentrations of some PFCAs, PFSA, PFMOPrA, PFPrOPrA, and PFMOAA may have increased after ozonation, possibly because of the oxidation of precursor compounds.²⁵ Disinfection with medium-pressure UV lamps and free chlorine (located between the BAC effluent and the finished water) may have decreased concentrations of PFMOAA, PFMOPrA, PFMOBA, and PFPrOPrA, but only to a limited extent. Small concentration changes between treatment processes may also be related to temporal changes in source water PFAS concentrations that occurred in the time frame corresponding to the hydraulic residence time of the DWTP.

Results in Figure 2 further illustrate that the PFAS signature of the August 2014 samples was similar to the mean PFAS signature observed during the 2013 sampling campaigns shown in Figure 1; i.e., PFPrOPrA concentrations (400–500 ng/L) greatly exceeded legacy PFAS concentrations. Moreover, three PFECAs (PFMOAA, PFO2HxA, and PFO3OA) exhibited peak areas 2–113 times greater than that of PFPrOPrA (Figure 2b).

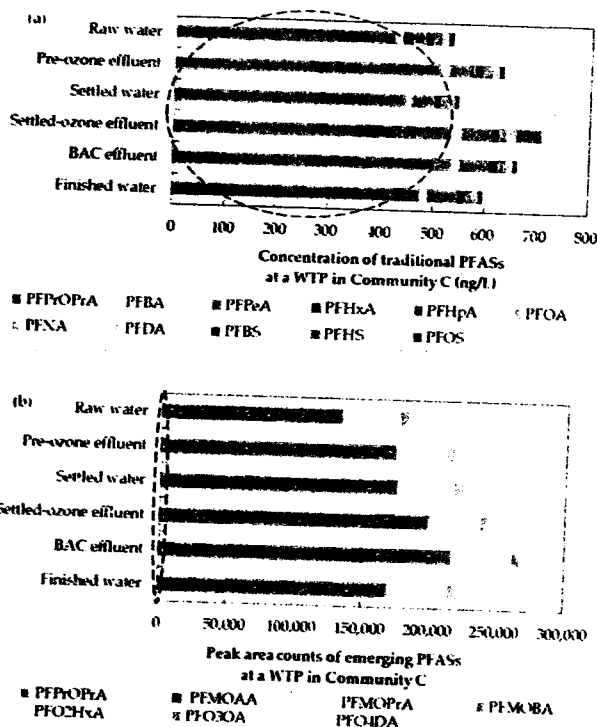


Figure 2. Fate of (a) legacy PFASs and PFPrOPrA and (b) PFECAs through a full-scale water treatment plant. Because authentic standards were not available for PFECAs other than PFPrOPrA, chromatographic peak area counts are shown in panel b. PFPrOPrA data are shown in both panels and highlighted with dashed ovals for reference. Compounds with concentrations below the QIs were not plotted.

The existence of high levels of emerging PFASs suggests a need for their incorporation into routine monitoring.

Adsorption of PFASs by PAC. PAC can effectively remove long-chain PFCAs and PFSA, but its effectiveness decreases with decreasing PFAS chain length.^{24,25,29} It is unclear, however, how the presence of ether group(s) in PFECAs impacts adsorbability. After a contact time of 1 h, a PAC dose of 100 mg/L achieved >80% removal of legacy PFCAs with total carbon chain lengths of ≥ 7 . At the same PAC dose, removals were 95% for PFO4DA and 54% for PFO3OA, but <40% for other PFECAs. Detailed removal percentage data as a function of PAC contact time are shown in Figure S5. There was no meaningful removal of PFMOBA or PFMOPrA, and the variability shown in Figure S5 is most likely associated with analytical variability. PFMOAA could not be quantified by the analytical method used for these experiments; however, on the basis of the observations that PFAS adsorption decreases with decreasing carbon chain length and that PFECAs with one or two more carbon atoms than PFMOAA (i.e., PFMOPrA and PFMOBA) exhibited negligible removal (Figure 3), it is expected that PFMOAA adsorption is also negligible under the tested conditions.

To compare the affinity of different PFASs for PAC, PFAS removal percentages were plotted as a function of PFAS chain length [the sum of carbon (including branched), ether oxygen, and sulfur atoms] (Figure 3b). The adsorbability of both legacy and emerging PFASs increased with increasing chain length. PFSA were more readily removed than PFCAs of matching chain length, a result that agrees with those of previous

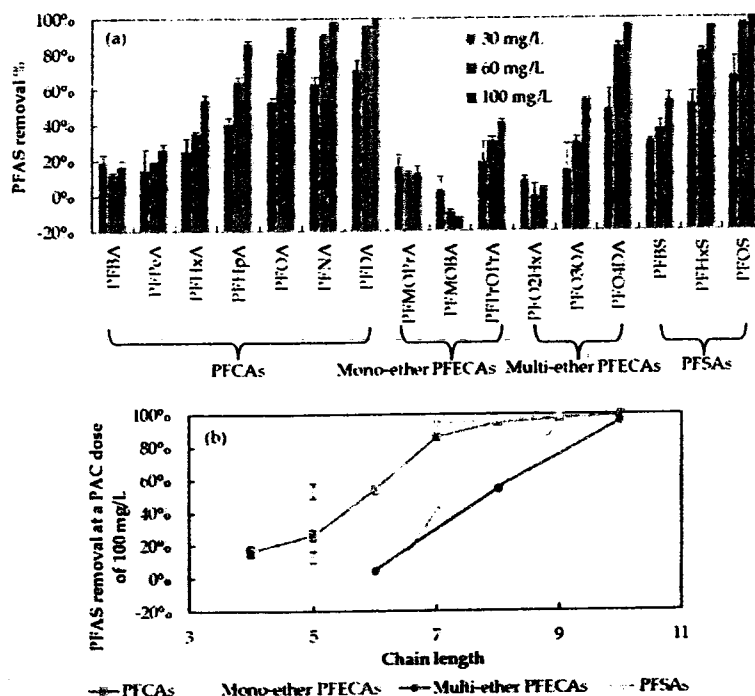


Figure 3. PFAS adsorption on PAC (a) at carbon doses of 30, 60, and 100 mg/L and (b) as a function of PFAS chain length. The PAC contact time in CFR water was 1 h. Legacy PFASs were spiked at ~ 1000 ng/L, and the emerging PFASs were at ambient concentrations. Figures show average PFAS removal percentages, and error bars show one standard deviation of replicate experiments.

studies.^{24,25,29} PFECAs exhibited adsorbabilities lower than those of PFCAs of the same chain length (e.g., PFMOBA < PFHxA), suggesting that the replacement of a CF_2 group with an ether oxygen atom decreases the affinity of PFASs for PAC. However, the replacement of additional CF_2 groups with ether groups resulted in small or negligible affinity changes among the studied PFECAs (e.g., PFMOBA \sim PFO2HxA, PFPrOPrA \sim PFO3OA). Alternatively, if only the number of perfluorinated carbons were considered as a basis of comparing adsorbability, the interpretation would be different. In that case, with the same number of perfluorinated carbons, PFCAs have an affinity for PAC higher than that of monoether PFECAs (e.g., PFPeA > PFMOBA) but an affinity lower than that of multi-ether PFECAs (e.g., PFPeA < PFO3OA).

To the best of our knowledge, this is the first paper reporting the behavior of recently identified PFECAs in water treatment processes. We show that PFECAs dominated the PFAS signature in a drinking water source downstream of a fluorochemical manufacturer and that PFECA removal by many conventional and advanced treatment processes was negligible. Our adsorption data further show that PFPrOPrA ("GenX") is less adsorbable than PFOA, which it is replacing. Thus, PFPrOPrA presents a greater drinking water treatment challenge than PFOA does. The detection of potentially high levels of PFECAs, the continued presence of high levels of legacy PFASs, and the difficulty of effectively removing legacy PFASs and PFECAs with many water treatment processes suggest the need for broader discharge control and contaminant monitoring.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00398.

Six tables, five figures, information about PFASs, analytical methods, and detailed results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: msun8@uncc.edu. Phone: 704-687-1723.

ORCID

Mei Sun: 0000-0001-5854-9862

Notes

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the USEPA.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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March 20, 2017

Monday

March 2017

Su	Mo	Tu	We	Th	Fr	Sa
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5	6	7	8	9	10	11
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April 2017

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MONDAY		Daily Task List
20		Arrange by: Due Date
7 AM		
8		
9		
10		
11	Knappe Paper Admin ConferenceRoom Frank Styers	
12 PM		
1	ARV Improvement Project Incident Action Plan ITConferenceRoom Kevin Knapp	Notes
2		
3	Long Range Planning Committee ITConferenceRoom Donna Pope	
4		
5		
6		

John Malone

April 19th

Presentation to CFPWA @ WTP

From: Ben Kearns
Sent: Thursday, April 13, 2017 9:19 AM
To: Jim Flechtner; Frank Styers; Carel Vandermeiden; Jim Tayson; Elizabeth Severt; William Roy; Craig Wilson; Allyson Ridout; Overby, Tommy D; 'heidi.cox@ncdenr.gov'; Steve Mongeau; Gary McSmith; Mike McGill; Justin Maurice; Eric Hatcher; Beth Eckert; Rebecca Cramer; Maggie Butler; Phil Brower
Cc: John Malone; Jacqueline Valade; Kevin Denson; Ken Vogt
Subject: Water Team Meeting PFOS/PFOA Presentation by Detlef Knappe
Attachments: 14D and PFAS Fate.docx

Hello All,

I have been approached by Detlef Knappe with NC State regarding legacy and emerging PFAS compounds in our raw water and their fate once they have passed through the Sweeney WTP treatment regime. Due to their persistent nature and potential concentrations in our source water, there is a strong desire to identify the PFAS compounds, their concentrations, and their fate in our treatment plants through a coordinated sampling effort with Detlef's lab. I have attached a short proposal outlining the project scope and desired sampling for the group to review. The scope of this project is such that thorough vetting and buy-in from all Authority levels would be best before anything moves forward.

Detlef and a colleague who specialize in the study of these PFAS compounds have been invited to come to the next Water Team Meeting on **Wednesday, April 19th at 1:00pm** to give a short presentation for the group. I felt this would be a great opportunity for all parties involved to discuss the nature of these compounds, their source(s), and what options we have as a utility for removal with subject matter experts. I believe that as a progressive leader amongst the utilities in the area, our path forward regarding these PFAS compounds should be a collective decision made with the health and safety of our customers in mind.

I hope that all who are on this e-mail can attend and feel free to contact me with questions if you cannot attend.

Best Regards,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

John Malone

From: Ben Kearns
Sent: Thursday, April 20, 2017 8:30 AM
To: Frank Styers; Beth Eckert; 'heidi.cox@ncdenr.gov'; Eric Hatcher; Jill Deaney; Phil Brower; Maggie Butler; Katherine Willis; Mike McGill; Justin Maurice; John Malone; Jacqueline Valade; Jim Tayson
Cc: Kevin Denson; Allyson Ridout
Subject: FW: Water Team PFAS Presentation attached
Attachments: PFAS_Wilmington_041917.pdf

Hello All,

Thank you for attending the water team meeting yesterday and allowing Detlef to present and field questions on the emerging contaminants of PFOS/PFOA & PFAS. Attached you will find the presentation from yesterday and feel free to share with those staff who you feel would benefit.

Best,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311

-----Original Message-----

From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Wednesday, April 19, 2017 2:52 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Presentation attached

Hi Ben,

Please see attached. Feel free to share with your staff.

Thank you,

Detlef

--

Detlef Knappe
Professor
319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering North Carolina State University Campus Box 7908
Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

TO: Ben Kearns
FROM: Detlef Knappe
SUBJECT: Fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle
DATE: April 12, 2017

Objective: Determine fate of 1,4-dioxane and perfluoroalkyl substances (PFASs) in the urban water cycle by tracing parcels of water through

- (1) The Sweeney water treatment plant
- (2) Wilmington's drinking water distribution system
- (3) Wilmington's sewage collection system
- (4) Wilmington's wastewater treatment plant

In addition, we are interested in evaluating the fate of 1,4-dioxane and PFASs during aquifer storage and recovery (ASR) as well as association of 1,4-dioxane and PFASs with biosolids.

Audience:

- (1) CFPWA staff: provide data demonstrating treatment challenges associated with emerging contaminants that occur at elevated levels in the Cape Fear River at Wilmington's drinking water intake. This information can be useful in efforts to control industrial sources of pollution upstream of Wilmington's drinking water intake.
- (2) Department of Environmental Quality staff: Since 2015, we have informed DEQ staff about the presence of contaminants in the Cape Fear River basin. Our goal is to encourage DEQ staff to control sources of pollution that affect downstream drinking water providers.

Background: Several unregulated contaminants occur at elevated levels in the Cape Fear River and its head waters (Haw and Deep Rivers). Among the constituents of concern are bromide, a disinfection by-product precursor, 1,4-dioxane, a likely human carcinogen, and perfluoroalkyl substances (PFASs) that are associated with a variety of adverse health outcomes, including cancer. The proposed study will focus on PFASs and 1,4-dioxane. The USEPA recently established a health advisory level for two PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), at 70 ng/L. While PFOA and PFOS levels at Wilmington's drinking water intake are low, the concentration of GenX, a replacement for PFOA, is in the 100s of ng/L. In addition, several other PFASs are present at even higher concentrations (Sun et al. 2016a). In addition, 1,4-dioxane occurs in Wilmington's source water at levels that exceed the North Carolina's stream water quality standard of 0.35 µg/L. Ozonation can indirectly oxidize 1,4-dioxane via the generation of hydroxyl radicals (Knappe et al. 2017). In previous sampling campaigns, we established that the ozonation processes at the Sweeney WTP are capable of oxidizing approximately two-thirds of the 1,4-dioxane coming into the plant (Knappe et al. 2017). In contrast, PFASs appear to pass through the Sweeney WTP without measurable attenuation (Sun et al. 2016a). In the previous sampling campaigns, we did not take into account hydraulic residence time such that we were not tracing the same parcel of water through the plant. Also, we did not establish 1,4-dioxane and PFAS fate once water leaves the Sweeney WTP.

Approach: To determine the fate of 1,4-dioxane and PFAS in Wilmington's urban water cycle, a PhD student supported by our National Science Foundation grant will work closely with CFPWA staff to track parcels of water through the Sweeney WTP, through Wilmington's drinking water distribution system, through Wilmington's sewage collection system, and Wilmington's wastewater treatment plant. We are already quite familiar with the Sweeney WTP, where we propose to take samples at the following locations:

- (1) Raw water intake,
- (2) Effluent of pre-ozone reactor,
- (3) Effluent of settling basin,
- (4) Effluent of settled water ozone reactor,
- (5) Effluent of GAC biofilter,
- (6) Effluent of UV reactor, and
- (7) Point-of-entry (POE) to distribution system (following contact with free chlorine)

We would need help from CFPUA staff to identify suitable sampling points in the drinking water distribution and sewage collection systems, and to estimate water ages at these sampling points. This information will be used to develop a sampling plan that permits tracking of water parcels through Wilmington's urban water cycle. Once the sampling plan is finalized, the PhD student, with support of a CFPUA staff member, will collect water samples at the locations and time points identified in the sampling plan. Samples for 1,4-dioxane analysis will be collected in 500-mL wide-mouth brown glass bottles according to EPA method 522 and stored at 4C until analysis. Samples for PFAS analysis will be collected in 1-L HDPE bottles and stored at room temperature until analysis.

In addition, we are interested in assessing the fate of 1,4-dioxane and PFASs in Wilmington's ASR system. Based on our understanding of Wilmington's ASR system, typical operation involves recharge of treated drinking water from Oct./Nov. through March, storage from March through June, and recovery from July through September. We propose to collect samples at the ASR well and at monitoring wells located 300, 450, 800, and 1,400 feet away from the ASR well. One option is to take monthly samples to determine concentrations of 1,4-dioxane and PFASs only. Another option, based on discussions we had with CFPUA 2.5 years ago, would be to conduct a more extensive study. In that case, the water quality (WQ) parameters shown in Table 1 could be monitored in the recharge water, during storage in the Upper Peedee aquifer, and during recovery. As indicated in Table 1, some WQ parameters will be monitored biweekly and others monthly, and analyses would be shared between CFPUA and NCSU as indicated in Table 1.

Table 1. Water quality monitoring parameters

Laboratory	Biweekly	Monthly
Cape Fear Public Utilities Authority	Temperature, pH, turbidity, specific conductance, dissolved oxygen, redox potential, residual chlorine (during recharge)	Total organic carbon, trihalomethanes
NCSU	Nitrate, nitrite, ammonium, sulfate, chloride, bromide, fluoride	1,4-dioxane, PFASs, dissolved organic carbon, UV ₂₅₄ absorbance

The monitoring results will illustrate to what extent 1,4-dioxane and PFAS concentrations (and also trihalomethanes) are attenuated during aquifer storage. Fluoride concentrations will be used as a tracer to quantify the extent of 1,4-dioxane and PFAS attenuation by dilution of recharge water with native groundwater. If attenuation occurs beyond that attributable to dilution, it will be related to redox conditions by measuring such parameters as redox potential, dissolved oxygen, nitrate, nitrite, ammonium, and sulfate.

Finally, we are interested in determining the partitioning of 1,4-dioxane and PFASs to biosolids. Currently, we are not familiar with the solids handling facilities at CFPUA's wastewater treatment plants. We would be looking for biosolids samples designated for land application. For the biosolids samples, we would measure 1,4-dioxane and PFAS concentrations in both the aqueous and solid phases. To accomplish this goal, we will separate the solids from the aqueous phase by centrifugation. The aqueous phase samples will be analyzed like any other water samples. The solid phase will be extracted with a 60/40 blend of acetonitrile/water (Washington et al. 2010), and we will measure 1,4-dioxane and PFAS levels in the solvent extracts. These two measurements will allow us to calculate partition coefficients describing the sorption of 1,4-dioxane and PFASs from water to biosolids.

Analytical methods

1,4-Dioxane concentrations will be determined by a recently developed GC/MS method in our laboratory (Sun et al. 2016b). PFAS concentrations will be determined by a LC-MS/MS method that targets approximately 20 PFASs, including perfluoroalkyl ether carboxylic acids that occur at high levels in Wilmington's source water (Sun et al. 2016a).

TOC/DOC will be measured by high-temperature combustion (Shimadzu TOC-VSCN analyzer) according to Standard Method 5310B. The concentration of UV-absorbing organic constituents will be measured at

a wavelength of 254 nm according to Standard Method 5910. Anion concentrations will be measured by ion chromatography using existing methods. NH_4^+ will be measured by colorimetric methods (Hach).

References

Knappe, D.R.U., Lopez-Velandia, C., Hopkins, Z., and Sun, M. Occurrence of 1,4-dioxane in the Cape Fear River watershed and effectiveness of water treatment options for 1,4-dioxane control. WRRF Final Report, 2017 (under review).

Sun, M., Arevalo, E., Strynar, M.J., Lindstrom, A.B., Richardson, M., Kearns, B., Smith, C., Pickett, A., and Knappe, D.R.U. "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina." *Environmental Science and Technology Letters*, 3(12): 415-419, 2016a.

Sun, M., Lopez-Velandia, C., and Knappe, D.R.U. "Determination of 1,4-dioxane in the Cape Fear River watershed by heated purge-and-trap preconcentration and gas chromatography-mass spectrometry." *Environmental Science and Technology*, 50(5): 2246-2254, 2016b.

Washington, J.W., Yoo, H., Ellington, J.J., Jenkins, T.M., and Libelo, E.L. "Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA." *Environmental Science and Technology*, 44(22): 8390-8396, 2010.

Beth Eckert

From: Jill Deaney
Sent: Monday, April 24, 2017 10:15 AM
To: Beth Eckert
Subject: FW: GenX Toxicity

From: Ben Kearns
Sent: Monday, April 24, 2017 8:37 AM
To: Jill Deaney <Jill.Deaney@cfpua.org>
Subject: FW: GenX Toxicity

FYI –

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Detlef Knappe [<mailto:knappe@ncsu.edu>]
Sent: Saturday, April 22, 2017 10:22 AM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: GenX Toxicity

Hi Ben,

I found the following abstract about GenX toxicity, which purports that GenX is more toxic than PFOA. GenX concentrations in Wilmington, Brunswick, and Pender greatly exceed the current health advisory level for PFOA. I think it is important that we push to dramatically reduce inputs of GenX and similar compounds into the Cape Fear River!

The work described below comes from one of the top PFAS research groups in the world (Ian Cousins at Stockholm University in Sweden).

Detlef

Comparing the potency in vivo of PFAS alternatives and their predecessors

Gomis Ferreira, Melissa Ines
Vestergren, Robin
Borg, Daniel

Abstract [en]

Since the year 2000, a number of per- and polyfluoroalkyl substances (PFASs) have been introduced onto the market to replace long-chain perfluoroalkyl acids (e.g. perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)) and their respective precursors. The main rationale for this industrial transition is that the PFAS alternatives are less bioaccumulative and toxic than their predecessors. Here, we evaluated to what extent differences in toxicological effect thresholds for PFASs, expressed as an administered dose, were confounded by differences in their distribution and elimination kinetics. Increased liver weight was selected as the investigated endpoint based on the availability of sufficient toxicological and toxicokinetic data to enable a comparison of sub-chronic effects. Converting administered doses into equivalent serum and liver concentrations significantly reduced the variability in the dose-response curves for perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (GenX). The toxicity ranking using serum (PFNA>GenX>PFOA>PFHxA>PFBA) and liver (GenX>PFNA≈PFOA≈PFHxA≈PFBA) concentrations also indicated that some PFAS alternatives may have a higher toxic potency than their predecessors when correcting for differences in toxicokinetics. For PFOS and perfluorobutane sulfonic acid (PFBS) the conversion from administered dose to serum concentration equivalents did not change the toxicity ranking which, however, could be due to the internal dose of PFBS being too low to allow a correct comparison. This study illustrates the importance of taking toxicokinetics/internal dose into account in substitution of hazardous chemicals for independent evaluation of bioaccumulation and toxicity criteria.

Keyword

PFOS, PFOA, PFAS alternatives, toxicokinetic model, potency, toxicity

National Category

Environmental Sciences

Research subject

Applied Environmental Science

Identifiers

urn:nbn:se:su:diva-141082 (URN)Available from: 2017-03-30 Created: 2017-03-30 Last updated: 2017-03-31Bibliographically approved

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Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering

North Carolina State University

Campus Box 7908

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Beth Eckert

From: Gregson, Jim <jim.gregson@ncdenr.gov>
Sent: Thursday, April 27, 2017 11:10 AM
To: Beth Eckert
Subject: RE: Npdes permitted
Attachments: NC0003573 Ownership Change.pdf; Ownership Change 2015.docx; Cover Ltr 2015.docx; 3573-fact sheet-2011.pdf

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section Division of Water Resources Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
Jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405

Email correspondence to and from this address is subject to the North Carolina Public Records Law and may be disclosed to third parties.

-----Original Message-----

From: Beth Eckert [mailto:Beth.Eckert@cfpua.org]
Sent: Wednesday, April 26, 2017 8:24 AM
To: Gregson, Jim <jim.gregson@ncdenr.gov>
Subject: Npdes permitted

Hey Jim

There is a manufacturing plant, Chemora, that discharges via NPDES permit into the cape fear river between here and Fayetteville. Is this group in your area and if so can I get a copy of there permit?

Beth Eckert

May 2, 2017

Tuesday

May 2017

Su	Mo	Tu	We	Th	Fr	Sa
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13	14	15	16	17	18	19
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27	28	29	30	31		

June 2017

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17	18	19	20	21	22	23
24	25	26	27	28	29	30

TUESDAY

2

ESI Membership Mtg. (raleigh, NC)

7 AM

8

9

Weekly Staff Meeting
Admin ConferenceRoom
Beth Eckert

10

Illegal Sewer Connection; Admin Confere

11

12 PM

1

Safety Incentive Gathering; EMD Break Room ; Latasha Edney

2

3

4

5

6

Daily Task List

Arrange by: Due Date

Notes

Beth Eckert

From: Ben Kearns
Sent: Tuesday, May 16, 2017 10:31 AM
To: Beth Eckert
Cc: John Malone
Subject: FW: Fwd: GenX in the Cape Fear River watershed

Hey Beth,

The below was sent to me by Detlef regarding inquiry from a Wilmington StarNews reporter, Vaughn Hagerty. His questions are aimed at the PFAS study Detlef presented on in the water team meeting. I do not feel that we have an obligation to answer any questions of his at this time due to the fact that it was Detlef's research, but having a discussion regarding what response we may need to provide to a news story would be prudent.

Thank you,

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Monday, May 15, 2017 6:10 PM
To: Ben Kearns <Ben.Kearns@cfpua.org>
Subject: Fwd: Fwd: GenX in the Cape Fear River watershed

Ben,
Please see below.
Detlef

My name is Vaughn Hagerty. I'm a journalist working on a story about PFASs, including GenX, in some drinking water systems in New Hanover and Brunswick counties. The story is for the Wilmington StarNews.

I came across "Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina" and was hoping you could help provide some important information and clarification for the article.

My initial questions are:

The paper labels the water treatment plants as A, B, C, and identifies a "fluorochemical manufacturer" upstream from C. Is treatment plant C the Cape Fear Public Utility Authority and is the manufacturer the Chemours (formerly DuPont) plant in Fayetteville? And your sampling took place in 2013?

I may be misreading but the paper also seems to state that treatment plant C's filtration was ineffective at removing GenX, or might have actually increased the concentration somehow? And the finished water (fig. 2a) contained levels of GenX similar to that of raw water? Is all of that correct?

Has any subsequent sampling and testing occurred? If so, could you elaborate on it or point me to someone who can? Is there any reason to believe that GenX either is or isn't still present in water from the Cape Fear downstream from the DuPont plant?

What does all this mean for people in the community served by C? Are the state or federal governments looking into this at all?

Can you speak at all about any potential health concerns? The searches I've done so far indicate that while the amount of research available on the potential health risks of GenX is small, at least some of it suggests it may have problems similar to that posed by PFOA. Can you address that or point me to someone who can?

Are you aware of any pictures that might have been taken during the sample gathering or other parts of the process that we might be able to publish? I'm looking for ways to illustrate the story.

Is there anyone else in North Carolina (or elsewhere) I should be speaking with about this?

I would sincerely appreciate any time you could spare to help me get this information. Let me know if there's anything else I could provide that would facilitate that.

Regards,

Vaughn Hagerty

Beth Eckert

From: Ben Kearns
Sent: Wednesday, May 17, 2017 3:51 PM
To: Frank Styers; Beth Eckert
Subject: FW: GenX Toxicity

I would also take a look at the bottom of the following link to the related list of papers surrounding the topic from the same group.

http://su.diva-portal.org/smash/record.jsf?aq2=%5B%5B%5D%5D&c=10&af=%5B%5D&searchType=LIST_COMING&query=&language=en&pid=diva2%3A1085404&aq=%5B%5B%5D%5D&sf=all&age=%5B%5D&sortOrder=author_sort_asc&onlyFullText=false&noOfRows=50&dswid=665

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Ben Kearns
Sent: Wednesday, May 17, 2017 3:48 PM
To: Frank Styers <frank.styers@cfpua.org>; Beth Eckert <beth.eckert@cfpua.org>
Subject: FW: GenX Toxicity

This was the abstract for the report. I have not yet gone and pulled the full research paper.

Ben Kearns
Surface Water Operations Supervisor
CFPUA Sweeney WTP
235 Government Center Drive
Wilmington, NC 28403
Office: 910-332-6577
Cell: 910-398-4311



From: Detlef Knappe [mailto:knappe@ncsu.edu]
Sent: Saturday, April 22, 2017 10:22 AM

To: Ben Kearns <Ben.Kearns@cfpua.org>

Subject: GenX Toxicity

Hi Ben,

I found the following abstract about GenX toxicity, which purports that GenX is more toxic than PFOA. GenX concentrations in Wilmington, Brunswick, and Pender greatly exceed the current health advisory level for PFOA. I think it is important that we push to dramatically reduce inputs of GenX and similar compounds into the Cape Fear River!

The work described below comes from one of the top PFAS research groups in the world (Ian Cousins at Stockholm University in Sweden).

Detlef

Comparing the potency in vivo of PFAS alternatives and their predecessors

Gomis Ferreira, Melissa Ines

Vestergren, Robin

Borg, Daniel

Cousins, Ian T.

(English)Manuscript (preprint) (Other academic)

Abstract [en]

Since the year 2000, a number of per- and polyfluoroalkyl substances (PFASs) have been introduced onto the market to replace long-chain perfluoroalkyl acids (e.g. perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA)) and their respective precursors. The main rationale for this industrial transition is that the PFAS alternatives are less bioaccumulative and toxic than their predecessors. Here, we evaluated to what extent differences in toxicological effect thresholds for PFASs, expressed as an administered dose, were confounded by differences in their distribution and elimination kinetics. Increased liver weight was selected as the investigated endpoint based on the availability of sufficient toxicological and toxicokinetic data to enable a comparison of sub-chronic effects. Converting administered doses into equivalent serum and liver concentrations significantly reduced the variability in the dose-response curves for perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoate (GenX). The toxicity ranking using serum (PFNA>GenX>PFOA>PFHxA>PFBA) and liver (GenX>PFNA≈PFOA≈PFHxA≈PFBA) concentrations also indicated that some PFAS alternatives may have a higher toxic potency than their predecessors when correcting for differences in toxicokinetics. For PFOS and perfluorobutane sulfonic acid (PFBS) the conversion from administered dose to serum concentration equivalents did not change the toxicity ranking which, however, could be due to the internal dose of PFBS being too low to allow a correct comparison. This study illustrates the importance of taking toxicokinetics/internal dose into account in substitution of hazardous chemicals for independent evaluation of bioaccumulation and toxicity criteria.

Keyword

PFOS, PFOA, PFAS alternatives, toxicokinetic model, potency, toxicity

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Detlef Knappe

Professor

319-E Mann Hall

Department of Civil, Construction, and Environmental Engineering

North Carolina State University

Campus Box 7908

Raleigh, NC 27695-7908

Phone: 919-515-8791

Fax: 919-515-7908

E-mail: knappe@ncsu.edu

Web page: <http://knappelab.wordpress.ncsu.edu/>

Beth Eckert

From: Frank Styers
Sent: Thursday, May 18, 2017 10:48 AM
To: Andrea Jordan
Cc: Beth Eckert
Subject: attorney client privileged
Attachments: PFOA.docx

Shiela Holman is the assistant secretary of the environment with NCDEQ.
Please place on Jim's letterhead.

Beth Eckert

From: Frank Styers
Sent: Thursday, June 1, 2017 4:11 PM
To: John Malone
Cc: Beth Eckert; Jim Flechtner
Subject: FW: Questions from StarNews re CFPUA

John,

Please provide answers to question numbers 2 and 3 below. Mr. Hagerty also requested to know if the water treatment process schematic that we currently have on our web site is accurate, but I have not been able to locate the schematic on our web site. Do you have a correct schematic we can provide or confirm that we do have one on the website that is accurate.

Thanks

Frank

From: Vaughn Hagerty [mailto:vaughn.hagerty@gmail.com]
Sent: Thursday, June 01, 2017 12:15 PM
To: Frank Styers <Frank.Styers@cfpua.org>
Subject: Questions from StarNews re CFPUA

Mr. Styers:

Thanks for taking the time to speak with me. Here are the questions we discussed:

- 1) My understanding is that CFPUA is not equipped to test for GenX on its own. Is that correct? Just fyi, Dr. Knappe indicated that this is the case and that few, if any, commercial labs in the U.S. are currently set up to do it. This is correct.
- 2) What percent of CFPUA's water does the Cape Fear River provide? Are all sources essentially mixed in the system? In other words, I get my water from CFPUA. When I turn on my tap, could that water be from the Cape Fear or groundwater or a mix of both or is it specific to where I live? John.
- 3) Can you provide a basic, layman's description of your water treatment system? Essentially, I'm asking about the basic processes you use. John.
- 4) What are CFPUA's current annual operating costs? The Authority's total operating cost for providing water and wastewater service is just under \$70 million annually.

Also, because I'm slightly OCD, just to be sure, I have you as: Frank Styers, CFPUA Chief Operations Officer Correct

Regards,

Vaughn Hagerty

P.S. In case you're wondering, the editors I'm working with at the StarNews are Gareth McGrath and Pam Sander

Beth Eckert

From: Gregson, Jim <jim.gregson@ncdenr.gov>
Sent: Thursday, June 8, 2017 1:35 PM
To: Beth Eckert
Subject: Gen x
Attachments: Evaluation+of+substances+used+in+the+GenX+technology+by+Chemours,
+Dordrecht.pdf

Jim Gregson
Regional Supervisor
Water Quality Regional Operations Section
Division of Water Resources
Department of Environmental Quality

910.796.7215 Reception Desk
910.796.7386 Direct
910.350.2004 Fax
Jim.gregson@ncdenr.gov

Wilmington Regional Office
127 Cardinal Drive Ext
Wilmington, NC 28405

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